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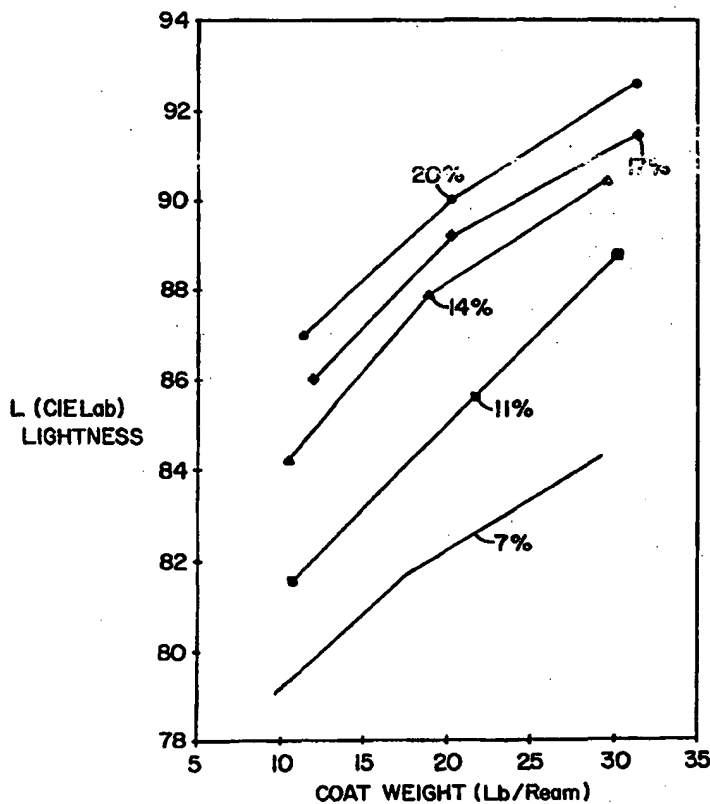
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: STABILIZED POLYOLEFIN COMPOSITION AND PROCESS FOR ITS PREPARATION

## (57) Abstract

This invention relates to new polyethylene compositions having improved extrusion characteristics and processes of reducing die lines, die build-up, and vapor line presence, thereby extending extrusion run times.



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TITLE OF THE INVENTION

STABILIZED POLYOLEFIN COMPOSITION AND PROCESS FOR ITS PREPARATION

CROSS-REFERENCE TO RELATED APPLICATION

This Application claims the benefit under 35 USC § 119(e) of Provisional Application Serial No. 60/032,654, filed December 9, 1996, Provisional Application Serial No. 60/039,588, filed February 28, 1997, Provisional Application Serial No. 60/046,970, filed May 19, 1997, Provisional Application Serial No. 60/048,490, filed June 3, 1997, and Provisional Application Serial No. 60/058,927, filed September 15, 1997.

FIELD OF THE INVENTION

This invention relates to polyolefin compositions useful for reduction or prevention of defects in extrusion coatings and films.

BACKGROUND OF THE INVENTION

Polyolefins are widely used in extrusion and molding applications, and in making films thereof. For example, polyethylene compositions are used in cast or tubular blown films, thin films, extrusion coated paper, paperboard, photographic paper, digital and thermal imaging papers, diaper backing, plastic substrates, injection or compression molded objects, packaging applications (such as coatings on soap boxes, milk cartons, fruit juice cartons, etc.), and the like. In these applications, the polymer is generally processed at high temperatures.

In the extrusion of polyethylene compositions into flat or tubular film or in the extrusion coating of

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paper or other substrates, particularly photographic paper, thermal and digital imaging paper, and diaper backings, there is frequently observed build-up in or on the die. This buildup causes marks and streaks in the coating or film which are known as die lines. These streaks can also cause holes or splits in the film. Build-up on the die may also change the geometry of the die exit causing undesirable surface roughness. Also droplets or debris from the build-up may break free and attach to the surface of the film or coating causing unsightly defects. Die build-up deleteriously affects both the appearance and mechanical properties of the polyethylene extrudate. In addition, further coatings on top of the die lines can also be affected, resulting in uneven coatings and appearance defects.

Build-up within the extruder is also known to be a problem and this frequently adds to the die build-up problems. Frequent build-up on the die is highly undesirable because it requires shutdown of the operation to clean out the extruder and the die. When die lines appear, the extrusion equipment must be stopped so that the die can be cleaned. If die lines appear frequently (shortly after start-up) then the equipment must be shut down often, dramatically increasing the cost of the material that is produced. These down times cause loss of production time and are economically undesirable.

The reasons for die build-up were not well understood. Certain additives normally used in polyolefins have an effect on die build-up, such as metal oxides, but die build-up can occur even without metal oxide additives. Although the present invention is not limited thereto, one type of composition having die build-up problems is polyethylene with titanium dioxide additive. Rutile and anatase types of titanium dioxide can cause die build-up problems, but in some

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instances and under certain conditions some types of titanium dioxide are worse than others. Both rutile and anatase titanium dioxide can be obtained with a variety of organic and/or inorganic coatings or surface treatments, such as an alumina coating. Depending on the type of titanium dioxide used and process applications, some formulations show die lines even after only 30 to 45 minutes of extrusion run time. Higher temperatures also exacerbate the problem.

10 It is known to control the die build-up problem in certain ways, i.e., to alter the process to reduce the production of die lines. For instance, die build-up problems and certain controls are discussed in J.D. Gander et al, "Review of Die Lip Build-Up In Plastic Extrusion", SPE ANTEC Meeting, Indianapolis, Indiana, 15 1996, and D.A. Holtzen et al, "Die Lip Plate-Out, A Proposed Mechanism", SPE RETEC Meeting, St. Louis, Missouri, 1996. These papers do not solve the problem of die lines nor do they, in particular, address or suggest modifying the extrusion compositions to 20 alleviate or overcome the problem.

A recent paper by D.E. Priester from DuPont Dow Elastomers L.L.C., "Reducing Die Build-Up in Extrusion Applications", POLYOLEFINS IX, Houston, 1995, Conference Proceedings, pp. 191-195, discusses the use of 25 fluoropolymers to reduce or eliminate die line build-up.

The article states that the addition of fluoropolymer is required to reduce die build-up, and teaches that the addition of a low molecular weight wax or products 30 containing a low molecular weight wax may actually increase the formation of die build-up and other surface problems.

More recently, in papers available at an April, 1997, ANTEC Conference in Toronto, Canada (Petiniot, 35 "New Generation of Anti-Die Deposit Masterbatches for White Polyethylene Films"; Spriet, "Recent Developments

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in Titanium Dioxide for White Masterbatches") it is noted that poor die line performance can be caused by surface defects on old dies, non-homogeneity of melts of polymer blends, the presence of waxes, increasing melt viscosity (e.g., by increasing pigment loading), and the presence of easily oxidizable resins.

Patents related to extrusion coatings in general include the following:

Japanese Patent 07126448 describes the use of polyethylene in combination with fatty acid salts plus phosphorus and/or phenolic antioxidants, and an amide;

Japanese Patent 05329992 teaches a composition containing polypropylene (85-95%), LDPE (5-20%), HDPE, peroxide, a phenolic antioxidant, and an aliphatic acid alkali metal salt or an alkaline earth metal salt;

EP App. No. 93113105.6 teaches an LLDPE packaging material containing carbon black and may include fatty acids (including stearic acid), fatty acid amides (including stearamide and erucamide), metal salts of fatty acids (including Mg, Ca, Zn, Zr, Ba) and bisamides;

Japanese Patent 06087984 teaches a polyolefin formulation containing a phosphorus compound, talc, an antiblocking agent, and a lubricant. The presence of titanium dioxide is not discussed;

DE 2727381 sets forth a polyethylene composition for biaxially stretched, blown film applications made with a Cr-containing catalyst, containing a phosphite stabilizer, a Ca, Zn, or K-containing salt of a C14-C22 fatty acid. The presence of titanium dioxide is not discussed;

U.S. 4,751,262 teaches an ethylene-acrylic acid interpolymer containing fatty acid amides wherein the polymer functional groups (e.g., carboxylic acid groups) may be neutralized with Zn, Na, Mg, K, Li, Ca, and Ba. Acrylic acid is an essential monomer in the polymer, and



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no titanium dioxide is mentioned;

U.S. 4,447,524 discusses alumina-coated  $\text{TiO}_2$  in a composition containing LDPE and 5-60 wt% HDPE for polyethylene-coated photographic paper. Additives such as slips and antioxidants, as well as Zn, Ca, Al, and Mg stearates, sodium palmitate, and sodium laurate are taught to be optional ingredients.

U.S. 4,219,453 sets forth inorganic filler-containing ethylene polymer film comprising 35-90% polyethylene, 10-65% 0.01-10 micron filler (which may include titanium dioxide and zinc oxide), 0.1 to 10 parts of a higher fatty acid, 0.5-15 parts metal salt of a higher fatty acid, and 0.05-5 parts of a phenolic stabilizer (parts based on weight of filler). The cation of the metal salts may be selected from Na, Li, Mg, Ca, and others, and the acids may be stearic, palmitic, lauric, and others;

U.S. 4,650,747 teaches a masterbatch containing 40-80% coated or uncoated anatase or rutile to let down for photographic paper coating. The use of Zn, Ca, Mg, Al, and Zr stearates, sodium palmitate, or sodium laurate is noted. It is also taught that the use of greater than 500 ppm (0.05%) of an antioxidant caused dye stains and microgrits;

U.S. 3,803,065 teaches the use of fatty acids, alcohols, amides, and metal salts of fatty acids, including Li, Na, K, and Zn as cations and stearic acid, are used to surface treat inorganics, e.g., silica, alumina, talc, clay, and calcium carbonate, to give antiblocking properties to clear films.  $\text{TiO}_2$  is not suggested;

U.S. Patent 5,173,397 describes a photographic support consisting essentially of a substrate and a resin layer, with the resin layer comprising a polyolefin resin, a titanium dioxide pigment, a fluorescent agent, and a color pigment or a color dye.

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The titanium dioxide is further defined by size of the particles and is said to be coated with 0.2 - 1.8 weight percent of an aluminum containing metal composition and 0 - 0.4 weight percent of a silicon composition. The working examples also show that the polyethylene compositions are based on a resin of 0.918 g/cc density, a melt index of 3.5 to 8.0 g/10 min. and the compositions contain 2.5 weight percent zinc stearate.

Mg, Ca, and Al stearates, Zr octylate, Na or Ca palmitate, and Na laurate are also mentioned;

U.S. 4,794,071 describes the use of Zn, Mg, Ca, and Al stearates, Zr octylate, Na and Ca palmitate, Na laurate, and Na, Ca, Mg, or Zn benzoate. The compositions describes therein also include "Hostalux-type" optical brighteners, white pigments (e.g,  $\text{TiO}_2$ ), and phenolic antioxidants. U.S. 4,859,539 describes similar compositions;

U.S. 3,411,908 mentions the use of aluminum stearate size on paper;

U.S. 3,501,298 mentions the use of oleylamide as a coating aid;

U.S. 4,169,188 notes that a dispersing agent selected from various types of surface active agents, higher aliphatic acids, and salts thereof, can be employed to improve pigment dispersibility;

U.S. 4,389,455 states that "it has been generally well known to add a surface active agent in the form of a metal soap such as calcium stearate or zinc palmitate in order to improve dispersibility of the titanium oxide pigment ...";

U.S. 5,049,595 is concerned with vented extruders and, in discussing the prior art, states that the methods are characterized by the use of auxiliary dispersing agents, "for example salts or esters of higher fatty acids, such as stearates, and the use of surface treated titanium dioxides." The patent itself

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is directed to dispensing with dispersing agents.

The formation of die lines is a function of several factors, including the type of  $\text{TiO}_2$  that is used (e.g., coated versus uncoated, surface treatment type, and particle size), temperature and rate of extrusion, interior surface composition and condition of the extruder, extruder die geometry, material viscosities, and volatiles, as outlined in the papers by Gander et al. and Holtzen et al., above. The literature in general, including the aforementioned patents and journal articles, focuses on improving die lines by making changes in processing conditions, equipment design,  $\text{TiO}_2$  type and degree of dispersion, base polyethylene viscosities, and fluoropolymer addition, and various additives, but these attempts have not completely solved the problem of die lines.

Moisture lines or vapor lines are also a problem in extrusion coatings. These are distinct from the die lines, and appear when volatile gases or exuded liquids exit the die along with the molten polymer. Good performance in both die lines and vapor lines is essential for a commercially acceptable extrusion coating formulation. Unless specifically noted herein, the terms moisture lines and vapor lines are used interchangeably herein.

In addition, there is the problem of high loadings of  $\text{TiO}_2$ . In the prior art, it is generally accepted that in a single coating only about 15 weight percent of the coating can be titanium dioxide (coated or uncoated). As a result of the inability to obtain higher loadings, several coatings are need to obtain opacity sufficient enough for certain purposes, particularly for coated substrates such as photographic and other imaging papers. This is highly inefficient and increases the complexity and cost of such coating processes.

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In light of the above, there is a need for polyolefin compositions and a process to modify polyolefin compositions so that they can be extruded into film or extrusion coated onto paper and other substrates without significant die build-up, die line and/or vapor line appearance in the extruded product even after many hours of operation at elevated temperatures. There is also a need for compositions that can contain high loadings of  $\text{TiO}_2$  so that a high amount (i.e., higher than 15 weight percent) of  $\text{TiO}_2$  can be put into a single coating onto a substrate.

The present inventors have surprisingly discovered that the aforementioned problems are addressed by the proper selection of additives in the polyolefin composition.

#### SUMMARY OF THE INVENTION

The present inventors have discovered compositions that provide reduced die line buildup and vapor line appearance and to compositions that result in high loadings of pigments such as  $\text{TiO}_2$  in a single coating, said compositions comprising a polyolefin and the proper selection of additives. The most critical and preferred additives according to the present invention are selected from a group including sulfur-containing phenolic antioxidants, sulfur-containing esters, and zinc or alkali metal salts of fatty acids, and combinations thereof.

The inventors have also discovered that for certain processes, including extrusion coating, film making, and molding processes wherein a polyolefin is extruded through one or more dies, die line formation and vapor line formation is reduced and/or extrusion time prior to onset of die line formation or vapor line formation is increased using the composition according to the present

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invention.

In addition, the inventors have discovered that altering the polyolefin additives composition, to compensate for die line accelerators, can reduce die line formation, vapor line problems, and/or increase extrusion time.

Futhermore, the inventors have discovered that the composition according to the present invention, with the proper selection of additives, allows for very high loadings of metal pigments (e.g.,  $\text{TiO}_2$  and/or  $\text{ZnO}$ ) in a single coating.

Thus, an object of the present invention is to describe compositions which may be extruded for extended periods without the formation of die lines and without the appearance of vapor lines.

Another object of the invention is to describe die line modification of an additives package to polyolefins to reduce the onset of die lines or to eliminate the presence of die lines in an extrusion coated substrate.

A further object of the invention is to describe polyolefin compositions capable of delivering high loadings of pigments such as titanium dioxide in a single coating.

Yet another object of the invention is to describe extrusion processes which can run for extended periods without the need for time-consuming shutdowns to clean the extruder equipment.

Still yet another object of the invention is to describe films and coated articles comprising the composition according to the present invention.

These and other objects, features, and advantages of the present invention will become apparent as reference is made to the following detailed description, preferred embodiments, specific examples, and the accompanying drawings.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates the effect of pigment loadings on die line onset times.

5 Figure 2 illustrates the logarithmic nature of the effect shown in Figure 1.

Figure 3 shows the effect of  $\text{TiO}_2$  loadings and coat weight on the lightness of coated Kraft paper.

10 Figure 4 shows the effect of  $\text{TiO}_2$  loadings and coat weight on the lightness of coated white paper.

Figure 5 shows the effect of  $\text{TiO}_2$  loadings and coat weight on hiding power.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

15

A preferred polyolefin formulation according to the present invention, for solving the die line problems, has stabilizers and chill roll release agents/slip additives, and does not contain metal soaps having calcium, magnesium, or aluminum as the counterion.

20 Another preferred polyolefin formulation according to the present invention, for solving the die line problems, has stabilizers and chill roll release agents/slip additives, and does not contain significant amounts of soaps that do not contain zinc or alkali

25 metals. In still another preferred polyolefin formulation for solving a vapor line problem, the formulation contains stearic acid. Yet another preferred polyolefin formulation contains zinc or alkali metal soaps. The compositions according to the present invention also preferably do not contain peroxides.

30 As used herein the terms "soap" is used synonymously with fatty acid salts and is preferably a C6-C36 fatty acid salt, more preferably a C8-C22 fatty acid salt, and may be linear or branched, and may be

35 saturated or contain unsaturation in the alkyl chain

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(e.g, erucic acid). As will become apparent below, the preferred cation in the fatty acid salts, in the composition according to the present invention, is selected from zinc, or alkali metals, and the preferred counterion is stearate. Furthermore, the materials described below are readily available commercially.

In the more preferred embodiment, the compositions contain at least one polyolefin (most preferably polyethylene) and one or more coated or uncoated pigments such as titanium dioxide or zinc oxide, and further comprise a sulfur containing phenolic antioxidant, such as Santonox®, in combination with a sulfur-containing ester, such as DSTDP (distearyl thiodipropionate) or Seenox® 412S. Optional ingredients include other stabilizers, such as phosphites, and other fillers and pigments such as talc or calcium carbonate.

In another more preferred embodiment, the compositions contain at least one polyolefin, most preferably polyethylene, and one or more coated or uncoated pigments such as titanium dioxide or zinc oxide, and further comprise at least one zinc or alkali metal salt of a fatty acid, such as zinc or sodium stearate, at least one stabilizer from either the phenolic antioxidant group (such as Santonox® or Irganox® 3114) or hindered amine light stabilizer (HALS) group. In this more preferred embodiment, preferred but optional additives include one or more of slips, such as PETS (pentaerythritol tetrastearate), mono-amides, such as erucamide or stearamide, bis-amides, such as Kemamide® W-40, fatty acids, such as stearic acid, phosphorus-containing stabilizers (such as Irgafos® 168 or Ultrinox® 626). Other optional additives include other fillers and pigments such as talc or calcium carbonate.

All of the above more preferred embodiments according to the present invention, in addition to

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providing for the aforementioned objects concerning die line formation and vapor line formation, also allow for exceptionally high loadings of pigments such as  $\text{TiO}_2$  or  $\text{ZnO}$ , e.g., greater than 15 weight percent, greater than 20 weight percent, or even higher than 30 weight percent (coated or uncoated weight added, based on the entire composition).

Furthermore, it is to be understood that the compositions according to the present invention may also contain colored dyes and pigments, optical whitening agents or other materials used to enhance the formulation's performance in its end-use environment, but which are not essential for achieving good die line performance, good vapor line performance, high loadings performance, or combinations thereof, achieved by the present invention. The skilled artisan, in possession of the present disclosure, can readily determine such necessary or preferred additional additives, and the amounts thereof, without undue experimentation.

In a photographic extrusion coating study, the typical ingredients required are low density polyethylene (LDPE),  $\text{TiO}_2$  for opacity and whiteness, polyolefin stabilizers and metal stearate chill roll release agents such as aluminum stearate or calcium stearate. When LDPE and alumina coated anatase  $\text{TiO}_2$  were extruded at 620°F on a paper coater, die lines appeared within two hours. When a stabilizer was added to the LDPE and the  $\text{TiO}_2$ , leaving the calcium- or aluminum-containing metal stearate out, the die line appearance was extended to four hours. When the metal stearate containing calcium, magnesium, or aluminum as the counterion was added to the LDPE and the  $\text{TiO}_2$ , leaving the stabilizer out, die lines appeared in three to four hours. By combining all three ingredients, that is the  $\text{TiO}_2$ , stabilizer and Ca-, Mg-, or Al-containing



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stearate, it was expected to be able to extrude without the appearance of die lines for up to six to 8 hours or perhaps more. However, die lines appeared after only one to two hours.

- 5       After further work, the metal stearate was identified as the key ingredient in the three way interaction and replacing the calcium-, magnesium-, or aluminum-containing metal stearate with another lubricant, such as either zinc stearate, lithium  
10       stearate, potassium stearate, or sodium stearate, greatly improved die line performance. In addition, further improvements were seen by changing the stabilizer package. In particular, Kronos® 1014 TiO<sub>2</sub> exhibited this improved die line performance behavior.  
15       Kronos® 1014 is an anatase titanium dioxide with a minimum of 95.0% TiO<sub>2</sub>, and additionally having alumina and organosiloxane, available from Kronos, Inc.

- Conventional polyethylene film and extrusion coating formulas containing titanium dioxide types that  
20       exhibit poor performance for die lines or die build up frequently can only be run for about 30 - 60 minutes before problems arise. This performance can be significantly improved through a process of modifying the polyethylene additives package. This improvement is  
25       achieved by the addition of a combination of stabilizers and chill roll release agents or slip additives.

- It is important to understand that, although the present invention is particularly directed to titanium dioxide-containing polyolefin composition, and more  
30       particularly to polyethylene with TiO<sub>2</sub> as an additive, it is concerned in general with die build-up and/or die line performance, and also to moisture or vapor line appearance, and therefore applies also to polyolefin compositions having other metal oxide additives, such as  
35       ZnO, to polyolefin compositions without metal oxide additives, to uses other than extrusion coating such as

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blown film and injection molding, and to uses with base material other than polyolefins, such as polyesters.

In a preferred embodiment of the process according to the present invention, an extrusion coating process  
5 is analyzed, inspected, or monitored for the production of die lines; if die lines appear too soon, then the polyethylene additives package is modified to replace any calcium-, magnesium, or aluminum-containing metal soap (e.g., calcium, magnesium, or aluminum stearate)  
10 with a zinc-, lithium-, potassium, or sodium-containing stearate or a non-metallic slip additive and extrusion coating the resulting composition. If no Ca-, Mg-, or Al-containing soap is present when die lines appear, a salt of a fatty acid, wherein the counterion is zinc,  
15 lithium, potassium, or sodium, or a non-metallic slip additive and/or a polyolefin stabilizer is added. The preferred additives package according to the present invention comprises a non-metallic slip additive or an alkali metal salt of a carboxylic acid, or a zinc salt  
20 of a carboxylic acid, more preferably an alkali metal or zinc salt of a fatty acid, even more preferably a sodium or zinc salt of a fatty acid, and most preferably zinc stearate or sodium stearate. In another preferred embodiment, this additives package also includes at  
25 least one polyolefin stabilizer, with the combination of a primary and secondary stabilizer being more preferred.

Likewise, die build-up and the presence of vapor lines can be monitored; any combination of die build-up, die line formation, and the presence of vapor lines can  
30 be monitored. The skilled artisan can determine when die build-up and/or die line formation and/or the presence of vapor lines occur. In these cases, the additives package can be modified in the same manner as the case for die line formation alone.

35 In a preferred embodiment of the extrusion coating composition according to the present invention, the

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composition comprises polyethylene,  $\text{TiO}_2$ , lubricant, and at least one polyolefin stabilizer. As used herein, the term lubricant means a chill roll release agent and/or a slip additive. Unless otherwise specified, the latter two terms are used interchangeably herein.

A very surprising discovery of the present inventors is that the extrusion coating composition according to the present invention may contain very high loadings of coated or uncoated titanium dioxide. Prior to the present invention, loadings above 15 weight percent in the final coating were impractical. The present invention allows for loadings in the final coating above 15 percent by weight (weight of the coated or uncoated  $\text{TiO}_2$  added), even more surprisingly from 20 percent by weight and above, still more surprisingly 30 weight percent and above. Generally, the limit of the metal oxide in polyethylene is about 85 weight percent, as discussed more fully below.

In a preferred embodiment, the extrusion coating composition includes loadings in the final coating (or film in the case of an extruded film) of metal oxide pigment (most preferably coated or uncoated titanium dioxide) from about 1 to 35 weight percent, more preferably 5 to 30 weight percent metal oxide pigment (if the pigment is coated, this would include the coat weight), about 0.003 to 10 weight percent lubricant (chill roll release agent/slip additive), more preferably 0.05 to 2.0 weight percent lubricant, even more preferably 0.05 to 1 weight percent lubricant, and about 0.003 to 1 weight % of at least one polyolefin stabilizer, more preferably about 0.005 to 0.3 weight percent stabilizer, most preferably 0.01 to 0.15 weight percent stabilizer, with the remainder being polyethylene. Optional additives are permitted. Weight percents are based on the total composition.

Generally for compositions according to the present

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invention, when they contain titanium oxide coated or uncoated grade, the amount of  $TiO_2$  is preferably about 1 to 35 weight %, more preferably about 3 to 35 weight %, still more preferably about 5 to 35 weight %, with about 5 to 15 weight percent being most preferred. In the case of the coated titanium dioxide, the weight percent includes the coating. However, as noted above, in some cases high loadings (e.g., above 15 weight percent) is the more preferred case.

10     The alkali metal salts of fatty acids are particularly effective in formulations containing alumina and silica-alumina coated titanium dioxide. In a preferred embodiment, the fatty acid salt contains 8 to 22 carbon atoms, more preferably 12 to 18 carbon atoms. In some cases it may be preferable to use mixtures of fatty acids, e.g., in the C12 to C18 range, it may be even more preferable to use mixtures of C16 and C18 in the fatty acid portion of the salt. Mixtures may be obtained by simple blending methods, or the mixtures may be commercially available.

At least one advantage of high loadings is that fewer coatings are required. Thus, in a preferred embodiment, articles according to the present invention comprise a substrate having three or fewer coatings, preferably two and even more preferably only one coating of the composition containing titanium dioxide.

25     A single coating that provides a high loading is also highly advantageous since it allows for the economical use of low grade paper such as Kraft paper, and various recycled papers, which may be turned into high quality paper with a single coating. The high loading is also particularly advantageous in package coating applications, such as soap boxes, milk boxes, and juice boxes, and in general for coating paperboard.

30     The term "stabilizers" per se is well known in the art. As used herein, the term "stabilizer" and

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"antioxidant" are used interchangeably. Examples of useful stabilizers in the present invention include alkylated phenols, bisphenols, and polyphenols, such as Irganox® 1076, Irganox® 3114, Ethanox® 330, Irganox® 1010, Naugard® XL-1, Cyanox® 1790, and the like, sulfur containing polyalkylated phenols, such as Irganox® 1035, Santonox® and the like, sulfur containing esters, such as distearyl thiodipropionate (DSTDP), dilauryl 3,3'-thiodipropionate (DLTDP) and the like, organic phosphites, such as Irgafos® 168, Ultranox® 626 and the like, and amines, such as Naugard® 445 and the like, and HALS (Hindered Amine Light Stabilizers) such as Chimassorb® 944. Another useful sulfur containing secondary stabilizer or costabilizer is Hostanox® SE-10 (dioctadecyl disulfide).

The terms "chill roll release agents" and "slip additives" are per se well-known in the art. Typically useful chill roll release agents and/or slip additives useful in the present invention include fatty acid amides, such as Kemamide® E, N-stearylceramide, stearamide and the like, complex esters, such as pentaerythritol tetrastearate (PETS), Myverol® 18-00K, Myverol® 18-06K and the like, fluoropolymers, such as Dynamar® FX-9613, Dynamar® FX-5920A and the like, natural and synthetic waxes, such as paraffin, microcrystalline wax, montan wax, polyethylene wax, oxidized polyethylene wax, chemically modified polyethylene wax and the like, and silicones, such as 4-7081, MB50-002, and the like. If desired, combinations of one or more stabilizers and one or more chill roll release agents or slip additives can be used.

Thus it was found that polyethylene formulations can be provided which have good uniformity, can be processed and extruded at elevated temperatures without die build-up or die line formation, and/or without the appearance of vapor or moisture lines, for extended

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periods, e.g., at least 8 hours, and which have significantly improved surface characteristics.

Preferred polyolefins are the polyethylenes.

Preferred polyethylenes include conventional low density polyethylenes (LDPE), high density polyethylenes (HDPE), linear low density polyethylenes (LLDPE) or mixtures of these polymers. The meaning of the terms LDPE, HDPE, and LLDPE are per se well-known in the art. Generally, the densities of these polyethylenes or their mixtures will range from about 0.900 to about 0.965 g/cc, although lower and higher density polyethylenes may be used. Useful materials preferably will also have melt index values of about 0.7 to about 50 g/10 min. In another embodiment, the polyolefin composition may be a mixture of polyolefins, such as a mixture of two polyethylenes having different melt indexes. A blend of two or more different base materials, such as polyethylene and polypropylene, or a polyolefin and a polyester, may also be used.

Base material concentrates, particularly polyethylene concentrates, can be prepared containing high concentrations of the stabilizers and chill roll release agents which can then be let down to the desired levels with additional base material (e.g., polyethylene). It is also possible to melt blend in only the final desired concentrations of the additives. Although not required, other additives including colorants, pigments, optical brighteners, dispersion aids and the like can be used if desired. The films and coatings of this invention generally are free of die defects for prolonged periods and have good surface appearance, good initial color, retain their color when aged under various lighting conditions and have good adhesion to paper.

The blends of this invention are readily prepared in conventional melt mixing apparatus such as, but not

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limited to, Banbury mixers, continuous compounders, single or twin screw extruders and the like. They can be extruded into film or extrusion coated onto substrates such as paper, paperboard, cardboard, other plastics and the like. In the extrusion coating of substrates, the coating may be on one or both sides.

It is also possible to coextrude these polyethylene compositions with other natural or colored polyethylenes, or other polymers such as polypropylene, propylene copolymers, ethylene copolymers with vinyl monomers such as vinyl acetate, methyl acrylate, ethyl acrylate and the like, polyesters, polyamides and the like. In an embodiment wherein a  $\text{TiO}_2$ -filled polyethylene having the stabilizers and slip additives is coextruded with a tie layer comprised of one or more different polymer(s), it is preferred that the at least one other polymer have adhesive properties to improve adhesion to the substrate. Particular examples of more preferred tie layers include polyolefins or modified polyolefins and/or Eastabonds, the latter of which is available from Eastman Chemical Company, Kingsport, TN.

These coextruded structures may contain two or more layers. In cases where three or more layers are present, the polyethylene compositions of this invention may be, for instance, the core or the outer layers.

A preferred example of this would be the coating of photographic paper with polyolefin extruded layers, rather than with a monolayer. This embodiment is not limited to photographic paper, but can be used with other coating resins, such as cellulosics, polyesters, copolyesters, and the like, for numerous purposes. It has particularly useful application where adhesion of a titanium dioxide filled resin is being coated onto the photographic paper, and prevention or minimization of die lines is desirable.

In another example of the preferred embodiment of

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coextrusion, a highly stable  $\text{TiO}_2$ -filled polyolefin top layer using a combination of primary and secondary antioxidants, such as Santonox® (a primary phenolic stabilizer/antioxidant) and DSTDP (a secondary sulfur containing ester stabilizer/antioxidant), in combination with a non-metallic stearate (such as PETS or HTSA) or an alkali metal stearate (such as sodium, potassium, or lithium stearate) is coextruded onto a substrate with a less stable polyolefin tie layer, the latter of which, in a more preferred embodiment is slightly oxidized, so that good adhesion of both polyolefin layers to each other and the tie layer to the substrate is obtained. In an even more preferred embodiment, the substrate, particularly paper when used as a component of photographic paper, is also oxidized to improve adhesion of the coextrudate thereto.

Suitable examples of oxidation processes are flame impingement, ozone exposure, and corona discharge, with corona discharge being more preferred. The aforementioned oxidation processes are within the purview of the skilled artisan.

Other desirable properties of a paper coated in this preferred coextrusion embodiment, such as curl, basis weight, opacity, brightness, and the like, can be obtained by other additives to the formulation, varying the amounts of additives, changing the coating weights, or resin types. This coextrusion dramatically improves the occurrence of die lines while simultaneously improving adhesion of the layers to the substrate, particularly paper and paper-containing substrates.

Typical processing and extrusion temperatures for these polyethylene compositions will generally be in the range of about 350 to about 650°F (177-343°C), but processes according to the present invention are not limited to such ranges.



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The improved compositions of this invention are useful in a wide range of applications including films, agricultural films, baby diapers, photographic paper, digital and thermal imaging paper, personal care and/or  
5 personal hygiene products, grocery and garbage bags, industrial films, carton stock, packaging applications such as milk and juice cartons and soap or juice boxes, hospital gowns, and the like.

When vapor lines appear, it has been found that the  
10 problem may be solved by adding, in a preferred embodiment, stearic acid. Other long-chain acids may be used, preferably those having 8 or more carbon atoms. Additionally, metal stearates and metal salts of other long chain acids, tackifying resins such as terpene-  
15 phenol resins, PEG waxes (those having a molecular weight of from about 600 to about 10,000), polyethylene waxes having carboxylic functionality such as olefin/maleic copolymers and oxidized polyolefins (e.g., those available from Eastman Chemical Company,  
20 Kingsport, TN), poly(vinyl alcohol), or more generally materials such as those enumerated having a polar end and a "fatty" segment, e.g., 8 or more carbon atoms, preferably C8-C22, may be used. Alternatively, the vapor line problem can be solved by the use of alkali  
25 metal stearates or zinc stearates.

The following examples will further illustrate the invention. Numerous modifications and variations are possible, and it is to be understood that within the scope of the appended claims, the invention may be  
30 practice otherwise than as specifically described herein.

**Example 1 (Comparative Example):**

A LDPE concentrate based on a LDPE having a density  
35 of 0.924 g/cc and a melt index of 4.2 g/10 minutes was prepared containing 45 weight % of Kronos 1014@ titanium

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dioxide (anatase  $\text{TiO}_2$  which is alumina coated with a siloxane surface treatment which is supplied by Kronos Inc.), 1.5 weight % of calcium stearate (chill roll release agent), 0.3 weight % DSTDP and 0.3 weight % Irgafos 168® (supplied by Ciba Co.) stabilizer. The ingredients were combined and processed in a 6 inch FARREL® continuous mixer and an 8 inch single screw extruder at 380°F and pelletized with an underwater pelletizer. The white polyethylene concentrate had a melt index of 2.5 g/10 min.

**Example 2 (Comparative Example):**

The polyethylene concentrate from Example 1 was pellet blended with natural LDPE pellets (density 0.924 g/cc; melt index 4.2 g/10 min.) at a ratio of 1:2 and the blend dried at 180°F for 12 hours in a desiccant bed dryer. The blend was fed to a clean Egan extruder (1.5 inch screw diameter; L/D ratio = 32:1) equipped with a clean 10 inch wide coat hanger die (die gap = 0.03 inches) used for paper coating experiments. The extruder was operated with extruder temperature settings ranging from 560°F at extruder zone 1 up to 595°F for zone 5. The adapter temperature was 595°F and the die was set at 580°F. The melt temperature coming from the die was 620-640°F. The white polyethylene melt was extruded at a rate of 30 pounds per hour onto 10 inch wide high quality white paper. Water in the chill roll was at a temperature of 60°F. The coating thickness on the paper was 25 microns. The coating operation was continued until die lines appear in the coating. This occurred within 60 minutes with this comparative composition.

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**Example 3:**

Using the procedure of Example 1, a white LDPE concentrate was prepared which contained 45 weight % of Kronos 1014® titanium dioxide, 0.3 weight % of DSTDP, 5 0.3 weight % Irgafos 168® (supplied by Ciba Co.), and 1.5 weight % of pentaerythritol tetrastearate (PETS). This concentrate was blended with natural polyethylene in a 1:2 ratio and extrusion coated onto paper as described in Example 2. A smooth, even, white coating 10 having good appearance was obtained and no die lines were observed even after 8 hours of coating.

Similarly good results are obtained when the concentrate is made with LDPE having a density of 0.921 g/cc and melt index of 1.7 g/10 min. or with a LDPE 15 having a density of 0.916 g/cc and a melt index of 20 g/10 min.

Similarly good results are obtained when a blend of 30 weight % LDPE and 70 weight % LLDPE having a melt index of 20 g/10 min. is used instead of LDPE alone. 20 Similarly good results are obtained when a blend of 90 weight % LDPE and 10 weight % HDPE is used instead of LDPE alone.

**Example 4:**

25 The concentrate of Example 3 is combined with natural LDPE polyethylene (melt index 4.2 g/10 min.) in a ratio of 1:10. This blend is processed in a blown film extruder at 450°F to prepare 1 mil tubular film. This white film has good appearance and is run for 8 30 hours without showing die lines.

**Examples 5 - 20:**

Using the procedure of Example 1, the compositions shown in Table 1A were prepared. These samples show 35 good performance in coating paper and can be run for

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extended periods of time without showing die lines.

**Example 21**

5 A low density polyethylene concentrate with 45 weight % alumina coated anatase TiO<sub>2</sub> (Kronos 1014® from Kronos Inc.), 0.3 weight % of a complex ester (pentaerythritol tetrastearate, "PETS"; Loxiol HOB-7119® from Hexcel) and 0.04 weight % of a thiopolyalkylated phenol (4,4'-thiobis(6-tert-butyl-m-cresol); Santonox®  
10 from Monsanto) and 0.1 weight % of a thio ester (distearylthiodipropionate; "DSTDP"; Evanstab 18® from Evans), is let down with LDPE in a 1:2 ratio with LDPE in a paper coater extruder at 620°F. The extruded film is free of die lines for at least 8 hours.

15 Subsequently, the same experiment was run, but using 0.2 weight % of a sulfur containing ester, and monitored until die lines appeared. Die lines did not appear until after 28 hours.

20 **Example 22**

A polyethylene concentrate with 70 weight % rutile TiO<sub>2</sub> (R104 from Dupont) is let down with LDPE to a final  
10 weight % TiO<sub>2</sub> on a cast film extruder at 500°F, and forms die lines within several hours. The time before  
25 die lines appear can be significantly extended to greater than 8 hours with the addition of a fatty acid amide (erucamide, Kemamide® E from Witco) at 1.5 weight % and two stabilizers, such as 0.2 weight % of an alkylidene polyphenol (Irganox® 3114 from Ciba Geigy)  
30 and 0.4 weight % of an organic phosphite (Ultranox® 626 from GE Specialty Chemicals) to the concentrate formulation.

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**Example 23**

A polyethylene formulation containing 10 weight % rutile  $\text{TiO}_2$  (R100 from Dupont) and 0.1 weight % primary stabilizer (2,6-di-t-butyl-p-cresol, Naugard® BHT from Uniroyal Chemical Company, Inc.) was extruded in a paper coater at 600°F, and forms die lines within a few hours.

The time before die lines appear can be significantly extended to greater than 8 hours with the addition of a fatty acid amide such as n-stearyl erucamide (HTSA® #3 from Hexcel) at 0.1 weight % and a primary and secondary stabilizer, such as 0.013 weight % of a polyalkylated phenol (Santonox®) and 0.07 weight % of a thio ester (DSTDP) to the formulation.

Subsequently, the same experiment as immediately above, using the addition of a fatty acid amide, and primary and secondary stabilizer, was run, except that Kronos® 1014 was substituted for the aforementioned R100, and the extrusion monitored until die lines appeared. Die lines did not appear until after 42 hrs.

The amount of additives used is a function of the amount of  $\text{TiO}_2$  in the polyethylene concentrate or in the fully compounded formula, the extrusion temperature, whether or not it must adhere to a substrate and whether or not it receives an additional coating, such as a photographic emulsion layer that must adhere to the polyethylene layer. Higher amounts of  $\text{TiO}_2$  may require greater amounts of slip/chill roll release agent. Higher extrusion temperatures may require greater amounts of stabilizer to negate the rate increase effect. Adherence to a substrate may require less stabilizer and additional coatings would require less slip/chill roll release agent. The additives chosen also take into consideration, cost, FDA needs, photoactivity, etc. depending on the end use customer needs. The proper amount of additives can be determined

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by the skilled artisan in possession of the present disclosure, based on operating conditions and intended use, without undue experimentation.

5   **Examples 24-231**

Also listed in Table 1B-1K are Examples 24-231, showing the use of additional compositions according to the present invention and comparative examples. These experiments were run according to the procedure of  
10   Example 1. The results are discussed further below in detail.

Table 1A

Weight % levels on this page are cut back 2:1 in polyethylene in the extrusion product.

		Wt %	type	Primary	Wt %	type	Secondary	Wt %	type	Secondary	Wt %	type	Slip	Wt %	Die Line Time
			stab	Stabilizer		stab	Stabilizer		stab	Stabilizer		s/p			onset/defined
	TiO <sub>2</sub>														
5	Kronos	45	2	Irganox 3114	0.1	5	DSTDP	0.2				1	HTSA	0.3	300 360
6	Kronos	45	2	Irganox 3114	0.1	6	Ultrinox 626	0.2				1	HTSA	0.3	360
7	Kronos	45	2	Irganox 3114	0.1				6	Irgafos 168	0.2	1	HTSA	0.3	270
8	Kronos	45	2	Irganox 3114	0.1	5	DSTDP	0.1	6	Irgafos 168	0.1	1	HTSA	0.3	240
9	Kronos	45	2	Irganox 3114	0.1	5	DSTDP	0.1	6	Ultrinox 626	0.1	1	HTSA	0.3	240
10	Kronos	45				5	DSTDP	0.3	6	Irgafos 168	0.3	2	PETS	1.5	510
11	Kronos	45				5	DSTDP	0.3	6	Irgafos 168	0.3	1	Kemamide E	1.5	450
12	Kronos	45	2	Irganox 3114	0.1	5	DSTDP	0.3	6	Ultrinox 626	0.3	2	PETS	0.3	300
13	Kronos	45	1	Irganox 1076	0.3							1	Kemamide E	1.5	300+
14	Kronos	45	2	Irganox 3114	0.1	5	DSTDP	0.2				1	Kemamide E	0.3	300
15	Kronos	45	2	Irganox 3114	0.1	6	Ultrinox 626	0.2				1	Kemamide E	0.3	240
16	Kronos	45	2	Irganox 3114	0.1	5	DSTDP	0.1	6	Ultrinox 626	0.1	1	Kemamide E	0.3	285
17	Kronos	45	3	Santonox	0.05							2	PETS	0.3	360
18	Kronos	45	3	Santonox	0.05	5	DSTDP	0.1	6	Ultrinox 626	0.1	2	PETS	0.3	455+
19	Kronos	45	3	Santonox	0.05				6	Ultrinox 626	0.2	2	PETS	0.3	360+
20	Kronos	45	2	Irganox 3114	0.1	5	DSTDP	0.1	6	Ultrinox 626	0.1	2	PETS	0.3	300

Table 1B

Weight % levels on this page are cut back 2:1 in polyethylene in the extrusion product.

	Wt %	type	Primary Stabilizer	Wt %	type	Secondary Stabilizer	Wt %	type	Secondary Stabilizer	Wt %	type	Slip	Wt %	Die Line Time onset defined
24 APG	50													90
25 Kronos	50													15
26 APG	45													90
27 APG	45	1	Irganox 1076	1.5							6	CaStearate	1.5	150
28 Kronos	45	1	Irganox 1076	1.5										180
29 Kronos	45													120
30 Kronos	45													90
31 Kronos	45										6	AlStearate 132	1.5	240
32 Kronos	45	2	Ethinox 330	0.32							6	AlStearate-dense	1.5	270
33 Kronos	45	2	Ethinox 330	0.28							6	CaStearate	1.5	210
34 Kronos	45	2	Irganox 1010	0.28										105
35 Kronos	45	1	Naugard BHT	0.32										240+
36 Kronos	45	2	Irganox 3114	0.32										240
37 Kronos	45	4	Naugard HM22	0.28										120
38 Kronos	45				5	DSTDP	0.28							270+
39 Kronos	45				5	DSTDP	0.28							150
40 Kronos	45				6	Ultranox 626	0.32							210
41 Kronos	45	3	Santonox	0.04										300
42 Kronos	45	2	Irganox 3114	0.1							1	HTSA	0.3	240+
43 Kronos	45	2	Irganox 3114	0.1	5	DSTDP	0.1				1	Kem E	0.3	450+
											1	Kem E	0.3	180



Table 1C

Weight % levels on this page are cut back 2:1 in polyethylene in the extrusion product.

	Wt %	type	Primary Stabilizer	Wt %	type	Secondary Stabilizer	Wt %	type	Secondary Stabilizer	Wt %	type	Slip	Wt %	Die Line Time
	TiO2				stab			stab			stab			onset defined
44	Kronos	45			5	DSTDP	0.1					1 Kemamide S-221	0.3	360
45	Kronos	45			5	DSTDP	0.1					1 HTSA	0.3	330
46	Kronos	45			5	DSTDP	0.1					1 Kemamide P-181	0.3	330
47	Kronos	45			5	DSTDP	0.1					1 Kemamide S-180	0.3	320
48	Kronos	45			5	DSTDP	0.1					1 Kemamide E-180	0.3	300
49	Kronos	45			5	DSTDP	0.1					1 Kemamide E-221	0.3	240
50	Kronos	45			5	DSTDP	0.1					1 Slip-eze	0.3	285
51	Kronos	45			5	DLTDP	0.1					2 PETS	0.3	180
52	Kronos	45			5	DSTDP	0.1					2 PETS	0.3	300
53	Kronos	45			5	DSTDP	0.1					2 Myvarol 18-06K	0.3	240
54	Kronos	45			5	DSTDP	0.1					2 Myvarol 18-06K	0.3	300
55	Kronos	45			5	DSTDP	0.1					4 Hoechst Wax E	0.3	270
56	Kronos	45			5	DSTDP	0.1					4 Epolene C13	0.3	240
57	Kronos	45			5	DSTDP	0.1					4 Ross Wax 100	0.3	230
58	Kronos	45			5	DSTDP	0.1					4 Petrolite PX100	0.3	180
59	Kronos	45			5	DSTDP	0.1					4 Hoechst PE520	0.3	200
60	Kronos	45			5	DSTDP	0.1					5200 fluid (silicone)	0.3	180 stopped
61	Kronos	45			5	DSTDP	0.1					5 200 fluid	0.3	255
62	Kronos	45			5	DSTDP	0.1					7 Almer 103	0.3	240 stopped
63	Kronos	45										3 fluoropol1	0.3	120
64	Kronos	45										3 fluoropol2	0.3	270
65	Kronos	45	3 Lowinox TBP6	0.1								2 PETS	0.3	150
66	Kronos	45	1 Irganox 1098	0.1								2 PETS	0.3	420
67	Kronos	45	2 Cyanox 1790	0.1								2 PETS	0.3	480
68	Kronos	45	3 Lowinox lbm6	0.04								2 PETS	0.3	300
69	Kronos	45	2 Naugard XL1	0.1								2 PETS	0.3	300
70	Kronos	45	2 Lowinox 44825	0.1								2 PETS	0.3	240
71	Kronos	45	3 Irganox 1035	0.1								2 PETS	0.3	210
72	Kronos	45	1 Lowinox WSP	0.1								2 PETS	0.3	180
73	Kronos	45	1 Lowinox 22M46	0.1								2 PETS	0.3	165
												2 PETS	0.3	90

Table 1D

Weight % levels on this page are cul back 2:1 in polyethylene in the extrusion product.

		Wt %	type	Primary Stabilizer	Wt %	type	Secondary Stabilizer	Wt %	type	Secondary Stabilizer	Wt %	type	Slip	Wt %	Die Line Time onset/defined
TiO2			stab			stab			stab			stab			
74 Kronos	45	3	Santonox	0.02	5	DSTDP	0.2						PETS	0.3	495+
75 Kronos	45	3	Santonox	0.04	5	DSTDP	0.2						PETS	0.3	480+
76 Kronos	45	3	Santonox	0.04	5	DSTDP	0.2						PETS	0.2	480+
77 Kronos	45	3	Santonox	0.04					6	Irganox 168	0.2		PETS	0.3	300
78 Kronos	45	1	Irganox 1098	0.1	5	DSTDP	0.2						PETS	0.3	240
79 Kronos	45	3	Lowinox TBM6	0.04	5	DLTDP	0.2						PETS	0.3	180
80 Kronos	45	2	Irganox 3114	0.1	5	DSTDP	0.2						PETS	0.3	180
81 Kronos	45	2	Irganox 3114	0.1					6	Ultranox 626	0.2		PETS	0.3	180
82 Kronos	45	1	Irganox 1098	0.1	5	DLTDP	0.2						PETS	0.3	180
83 Kronos	45	2	Irganox 3114	0.1					6	Irganox 168	0.2		PETS	0.3	120
84 Kronos	45	2	Cyanox 1790	0.1	5	DSTDP	0.2						PETS	0.3	120
85 Kronos	45	2	Ethanolox 330	0.1	5	DSTDP	0.2						PETS	0.3	60
86 Kronos	45				5	DSTDP	0.2						PETS	0.3	300
87 Kronos	45				5	DSTDP	0.08						PETS	0.3	215
88 Kronos	45	2	Irganox 3114	0.1	5	DSTDP	0.1						PETS	0.3	180
89 Kronos	45	1	Irganox 1076	0.28					6	Irganox 168	0.1		PETS	0.3	205
90 Kronos	45				5	DSTDP	0.28						PETS	1.5	150
91 Kronos	45	2	Ethanolox 330	0.15	5	DSTDP	0.15						AlStearate 132	1.5	120
92 Kronos	45				5	DSTDP	0.28						AlStearate 132	1.5	90
93 Kronos	45				5	DSTDP	0.1						AlStearate-dense	1.5	90
94 Kronos	45				5	DSTDP	0.28						Zinc Stearate	0.5	120
95 Kronos	45	2	Ethanolox 330	0.15					6	Irganox 168	0.15		CaStearate	1.5	120
96 Kronos	45	2	Irganox 3114	0.28					6	Irganox 168	0.28		CaStearate	1.5	60
97 Kronos	45				6	Ultranox 626	0.28						CaStearate	1.5	90
98 Kronos	45				5	DSTDP	0.28						CaStearate	1.5	180
99 Kronos	45				5	DSTDP	0.28						CaStearate	0.8	90
100 Kronos	45	3	Santonox	0.04									CaStearate	0.4	60+
													CaStearate	0.3	120

Table 1E  
Weight % levels on this page are final % in the extrusion product.

		Wt	type	Primary	Wt	type	Secondary	Wt	type	Secondary	Wt	type	Slip	Wt	Die Line Time
	TiO2	%	stab	Stabilizer	%	stab	Stabilizer	%	stab	Stabilizer	%	stab		%	onset defined
101	Kronos	20													60
102	Kronos	15													100
103	Kronos	10													270
104	Kronos	5													660
															685+
	Rutile TiO2														
105	R100	20													120
106	R100	15													480
107	R100	12													180+
108	R100	15	1	Irganox 1076	0.1							6	CaStearate	0.5	60
109	R100	15	3	Santonox	0.01	5	DSTDP	0.03				2	PETS	0.1	300+
110	R104	15													225
111	R104	20													150
112	R104	15	3	Santonox	0.01	5	DSTDP	0.03				2	PETS	0.1	540+
113	RCL188	20													150
114	RCL188	15													240+

Onset Die Line Time: first indication of die lines in the extrusion  
Defined Die Line Time: Clearly established die lines in the extrusion  
Kronos = Kronos 1014

Table 1F

Weight % levels on this page are cut back 2:1 in polyethylene in the extrusion product.

	TiO2	Wt %	Primary Stabilizer	Wt %	Secondary Stabilizer	Wt %	Slip	Wt %	Die Line Time
			type stab	type stab	type stab	type stab	type stab	type stab	onset defined
115	APG	45							240 300
116	Kronos	45	3 Santonox	0.04					180 240+
117	Kronos	45	3 Lowinox TBM6	0.1					480
118	Kronos	45		5 DSTDP	0.2		2 PETS	0.3	240 300
119	Kronos	45	3 Santonox	0.04	5 DSTDP	0.2			600 720+
120	Kronos	45					2 PETS	0.3	180 210
121	Kronos	45					1 HTSA	0.3	150
122	Kronos	45		5 DSTDP	0.1		1 Kemamide W-40	0.3	360 420
123	Kronos	45		5 DSTDP	0.1		1 Kemamide B	0.3	300 360
124	Kronos	45		5 DSTDP	0.1		1 Kemamide E	0.3	120
125	Kronos	45		5 Seenox 412S	0.1		2 PETS	0.3	360 470
126	Kronos	45	7 Hostanox osp1	0.1					300+
127	Kronos	45		5 Hostanox se10	0.1				120 180
128	Kronos	45		5 DSTDP	0.1		6 Zinc Stearate	1.5	480+
129	Kronos	45		5 DSTDP	0.1		6 Zinc Stearate	2.5	420+
130	Kronos	45					3 Zinc Stearate	1.5	630+

Table 1G

Weight % levels on this page are cut back 2:1 in polyethylene in the extrusion product.

Weight % levels on this page are cut back 2.1 in polyethylene in the extrusion product.																	
		Wt	Primary	Wt	Secondary	Wt	type	Secondary	Wt	type	Slip	Wt	type	Slip	Wt	Die Line Time	
	TiO2	%	stab	Stabilizer	%	stab	Stabilizer	%	stab	Stabilizer	%	stab	Stabilizer	%	stab	onset defined	
131	Kronos	45												1	Kemamide B	0.3	300
132	Kronos	45												1	Kemamide W-40	0.3	180
133	Kronos	45												1	Kemamide S-180	0.3	120
134	Kronos	45												1	Kemamide S-221	0.3	120
135	Kronos	45	7	Hostanox osp1	0.1											300+	
136	Kronos	45				5	Hostanox se10	0.1								120	
137	Kronos	45	7	Hostanox osp1	0.1	5	Hostanox se10	0.1								300	
138	Kronos	45	3	Santonox	0.04	5	DSTDP	0.2						6	Zinc Stearate	1.5	720+
139	Kronos	45	3	Lowinox TBP6	0.1	5	Seenox 412S	0.1						1	Kemamide W-40	0.3	720+
140	Kronos	45	3	Lowinox TBP6	0.1	5	Seenox 412S	0.1						6	Zinc Stearate	1.5	720+
141	Kronos	45	3	Lowinox TBM6	0.1	5	Seenox 412S	0.1						1	Kemamide W-40	0.3	600+
142	Kronos	45	3	Lowinox TBM6	0.1	5	Seenox 412S	0.1						6	Zinc Stearate	1.5	720+
143	Kronos	45	7	Hostanox osp1	0.1	5	Seenox 412S	0.1						1	Kemamide W-40	0.3	480
144	Kronos	45	7	Hostanox osp1	0.1	5	Seenox 412S	0.1						6	Zinc Stearate	1.5	720
145	Kronos	45	3	Santonox	0.04	5	DSTDP	0.2	8	stearic acid	0.5			2	PETS	0.3	660+
146	Kronos	45	1	Irganox 1076	0.28									6	Zinc Stearate	1.5	480

Trial 145 greatly improved for vapor lines, even coating

Trials with zinc stearate greatly improved for vapor lines, even coating

Wt % levels for 147 - 174 are cut back 2:1 in polyethylene in the extrusion product. Wt % levels for 175 - 181 are final % in the extrusion product.

[illegible]

Table 11

Weight % levels are cut back 2:1 in polyethylene in the extrusion product.

		Wt %	type	Primary Stabilizer	Wt %	type	Secondary Stabilizer	Wt %	type	Secondary Stabilizer	Wt %	type	Slip	Wt %	Die Line Time onset defined
	TiO <sub>2</sub>		stab			stab						stab			540+
182	CaCO <sub>3</sub>	60													540+
183	Kronos	60	8	Chlmassorb 944	0.3										180
184	RCL188	60	8	Chlmassorb 944	0.3										600
185	Kronos	45	1	Lowinox 22M46	0.1	5	DSTDP	0.1							120
186	Kronos	45	2	Lowinox 44B25	0.1	5	DSTDP	0.1							120
187	Kronos	45	3	Lowinox 1bm6	0.04	5	DSTDP	0.2	(Lowinox ground into a powder)						420
188	Kronos	45	3	Lowinox 1bm6	0.1	5	DSTDP	0.2							240
189	Kronos	45	3	Santonox	0.1	5	DSTDP	0.2							420
190	APG	36	11	Zinc Oxide	9										240
191	Kronos	45						10 diatomaceous earth	1.2			1	Kemamide E	0.6	300
192	Kronos	45	3	Santonox	0.04							1	Kemamide W-40	0.1	180
193	Kronos	48	3	Santonox	0.04	5	DSTDP	0.2				2	PETS	0.3	240

Table 1J

Weight % levels are cut back 2:1 in polyethylene in the extrusion product.

	TiO <sub>2</sub>	Wt %	Primary Stabilizer	Wt %	Secondary Stabilizer	Wt %	Secondary Stabilizer	Wt %	Slip	Wt %	Die Line Time onset	Die Line Time defined
194 Kronos	45	8	Chimassorb 944	0.3					6	K stearate	1.5	720
195 Kronos	60	8	Chimassorb 944	0.3					6	K stearate	2.5	780
196 Kronos	45	2	Irganox 3114	0.1	5	DSTDP	0.1		6	K stearate	1.5	840+
197 Kronos	45	8	Chimassorb 944	0.3					6	LI Stearate	1.5	780+
198 Kronos	45	2	Irganox 3114	0.1	5	DSTDP	0.1		6	LI Stearate	1.5	60
199 Kronos	60	8	Chimassorb 944	0.3					6	Na benzoate	2.5	600+
NOTE: Run 199 ran well for die line performance, but had many undispersed sodium benzoate particles in the extrusion finish, making it unacceptable overall. Based on Run 183 with Chimassorb 944 failing at 3 hours, it can be concluded that enough sodium benzoate was dispersed to help die lines.												
200 APG	60	8	Chimassorb 944	0.3					6	Na Stearate	1.5	600
201 APG	60	8	Chimassorb 944	0.3					6	Na Stearate	2.5	420
202 Kronos	45	8	Chimassorb 944	0.3					6	Na Stearate	1.5	1260
203 Kronos	45	8	Chimassorb 944	0.3					6	Na Stearate	1.5	1440+
204 Kronos	45	8	Chimassorb 944	0.3	5	DSTDP	0.1		6	Na Stearate	1.5	600+
205 Kronos	45	8	Chimassorb 944	0.3	5	DSTDP	0.1	2	Irganox 3114	0.04	600	
206 Kronos	45	8	Chimassorb 944	0.3				2	Irganox 3114	0.1	600+	
207 Kronos	60	8	Chimassorb 944	0.3					6	Na Stearate	1.5	600+
208 RCL188	60	8	Chimassorb 944	0.3					6	Na Stearate	2.5	360
209 Kronos	45	2	Irganox 3114	0.1	5	DSTDP	0.1		6	Na Stearate	2.5	540+
210 Kronos	60	2	Irganox 3114	0.04	5	DSTDP	0.1		6	Na Stearate	1.5	960
211 R100	60	2	Irganox 3114	0.04	5	DSTDP	0.1		6	Na Stearate	1.5	60
212 Kronos	45	3	Santinox	0.04	5	Seenox 412S	0.1		6	Na Stearate	1.5	600+
213 Kronos	45							1	Kem. W-40	0.1	480+	
214 Kronos	60								6	Na Stearate	1.5	540+
									6	Na Stearate	2.5	720+



Table 1K

Weight % levels on runs 215 - 230 are cut back 2:1 in polyethylene in the extrusion product.

	Wt %	Wt type stab	Primary Stabilizer	Wt %	Wt type stab	Secondary Stabilizer	Wt %	Wt type stab	Secondary Stabilizer	Wt %	Wt type stab	Slip	Wt %	Die Line Time onset/defined
215 Kronos	60	8	Chimassorb 944	0.3								6 Zinc Stearate	1.5	60 120
216 R100	60	8	Chimassorb 944	0.3								6 Zinc Stearate	1.5	660+
217 RCL188	60	8	Chimassorb 944	0.3								6 Zinc Stearate	1.5	660+
218 Kronos	45	2	Irganox 1010	0.1				6	Irganox 168	0.2		6 Zinc Stearate	1.5	120 180
219 Kronos	45	2	Irganox 3114	0.1	5	DSTDP	0.1					6 Zinc Stearate	1.5	120 180
220 Kronos	60	2	Irganox 3114	0.1	5	DSTDP	0.1					6 Zinc Stearate	1.5	60 60
221 Kronos	60	2	Irganox 3114	0.1	5	DSTDP	0.1					6 Zinc Stearate	2.5	300
222 Kronos	60	2	Irganox 3114	0.1	5	DSTDP	0.1	6	Na stearate	1		6 Zinc Stearate	1.5	240
223 Kronos	60	2	Irganox 3114	0.1	5	DSTDP	0.1	8	stearic acid	0.5		6 Zinc Stearate	2	180
224 R100	60	2	Irganox 3114	0.1	5	DSTDP	0.1					6 Zinc Stearate	1.5	660
225 RCL188	60	2	Irganox 3114	0.1	5	DSTDP	0.1					6 Zinc Stearate	1.5	120 180
226 Kronos	45	3	Lowinox 1bm6	0.1	5	Seenox 412S	0.1					6 Zinc Stearate	1.5	780+
227 Kronos	45	3	Santonox	0.04	5	DSTDP	0.2					6 Zinc Stearate	1.5	720+
228 Kronos	45	3	Santonox	0.04	5	DSTDP	0.2					6 Zinc Stearate	1.5	300 360
229 Kronos	45	3	Santonox	0.04	5	DSTDP	0.2					6 Zinc Stearate	1.5	120 180
230 Kronos	45	3	Santonox	0.04	5	DSTDP	0.2					6 Zinc Stearate	1.5	180 180
Run 231 was cut back 1:1 in polyethylene for a final 30 weight percent TiO2														
231 Kronos	60	8	Chimassorb 944	0.3								6 Na Stearate	2.5	480+

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The metal oxide contemplated in the polyethylene composition according to the present invention can be any metal oxide in any form, coated or uncoated, and for most purposes will be a metal oxide pigment, such as titanium dioxide or zinc oxide. In a more preferred embodiment, the metal oxide is coated or uncoated  $\text{TiO}_2$ , even more preferably coated anatase or rutile, and still more preferably alumina coated anatase or rutile. In a preferred embodiment, the coating on titanium is alumina or a silica-alumina coating.

In the preferred embodiment,  $\text{TiO}_2$  content in polyethylene can vary from 1 weight % (or below) to 85 weight %, where it reaches the critical pigment volume concentration, which is the point where the polyethylene can no longer surround the pigment particle completely during melt compounding. Stabilizer levels preferably range from 0.003 weight % to 1.0 weight %, depending on the effectiveness of the stabilizer and the above stated considerations. Chill roll release agents/slip additives preferably range from 0.003 weight % to 10 weight % depending on the above stated considerations and whether or not it is added as part of a concentrate or as a fully compounded formula. In a more preferred embodiment, final composition at the extrusion die can vary from 1 weight % to 25 weight % for  $\text{TiO}_2$ , from 0.003 weight % to 0.5 weight % for primary and secondary stabilizers, and from 0.003 weight % to 3 weight % for chill roll release agents/slip additives.

Compositions according to the present invention allow for unusually high loadings of pigments such as titanium dioxide and zinc oxide. Since high loadings in a single coating can be achieved, a lower grade of paper, such as Kraft, recycled, and/or unbleached paper, can be used.

As shown in Figure 1, as the percent of  $\text{TiO}_2$  is increased in a given polyethylene composition

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(containing no other additives), the onset of die lines appears much sooner. The effect is nearly logarithmic, as shown in Figure 2. These two tables show that, while increased loadings of metal oxide pigments are good for opacity, die line performance is not commercially acceptable.

Figure 3 shows the effect of  $\text{TiO}_2$  loadings and coating weight on  $L^*$  using Kraft Paper. ( $L^*$  is a standard measurement of Lightness, well known to the person of ordinary skill in the art). A series of extrusion coatings of titanium dioxide in polyethylene (and no other additives) were made onto Kraft (brown, unbleached) paper to see the effect of  $\text{TiO}_2$  loading (weight percents) and coating weight (thickness) on the lightness of the final product. The formulations were comprised of the given weight percent of Dupont R100 uncoated rutile titanium dioxide, with the remainder being LDPE. The statistical regression model for this data is  $L^* = 72.698 + (0.574 \times [\% \text{TiO}_2]) + (0.299 \times [\text{coat wt.}])$  with  $r^2 \text{ adj} = 0.962$ .

It was heretofore generally recognized that 15 weight percent of  $\text{TiO}_2$  was the practical coating limit before die lines became a significant downtime factor. Coating producers who wanted the opacity of 20 weight percent  $\text{TiO}_2$  would run two extrusions of 10 weight percent  $\text{TiO}_2$  to achieve the effect. Using the predictive model, 10 weight percent  $\text{TiO}_2$  at 10 lb/ream gives an  $L^*$  of 81.4. At double the coat weight, or the equivalent of two coatings, the predicted  $L^*$  is 84.4. At 20 weight percent  $\text{TiO}_2$  the predicted  $L^*$  is 87.1 at 10 lb/ream, indicating that with the same amount of  $\text{TiO}_2$ , all in one coating, a higher  $L^*$  can be achieved. An equivalent  $L^*$  of 84.4 could be achieved at the 10 lb/ream using 15.2 weight percent  $\text{TiO}_2$ . Compositions according to the present invention follow the predictive model without exhibiting the same die defects exhibited

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by the polyethylene/TiO<sub>2</sub> composition. Therefore, it is now possible to use less TiO<sub>2</sub>, obtain thinner coatings and eliminate an entire extrusion step (i.e., the second coating), by using compositions according to the present invention.

Figure 4 shows the results of the same experiment as in Figure 3, but using white paper instead of Kraft paper. While the effect when coating onto white paper is not as dramatic as it is coating onto brown paper, the trends are similar and significant. The statistical regression model for this data is  $L^* = 92.211 + (0.104 \times [\%TiO_2]) + (0.068 \times [\text{coat wt.}])$ , with  $r^2 \text{ adj} = 0.958$ .

In this case, at 10 weight percent TiO<sub>2</sub> and 10 lb/ream, the predicted L\* is 93.9. Increasing TiO<sub>2</sub> to 20 weight percent at the same coating weight, the predicted L\* is 95. The model predicts that it would take a coating thickness of 25.3 to achieve the same L\* with 10 weight percent TiO<sub>2</sub>, which would require 25% more TiO<sub>2</sub> and also result in thicker coated paper. This also can have a negative impact if the paper is intended for a personal computer printer where feeding paper to the printer is dependent on thickness. Another advantage of being able to coat a higher loading of TiO<sub>2</sub> at a reduced thickness is that paper that is less bright can be used (less bleaching of the pulp) and the TiO<sub>2</sub> can do the work to achieve the final L\*. Since the heretofore acceptable limit of practical coating load is 15 weight percent, and compositions according to the present invention follow the predictive model without exhibiting die defects as in the polyethylene/TiO<sub>2</sub> compositions, higher loads can be run using formulations according to the present invention to boost the achievable L\* by as much as 0.5 units.

Figure 5 shows the results of the same experiments run for Figure 4, showing the effect on contrast ratio, which is a form of opacity measurement. The test is

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performed using ASTM D2805-95, which is the standard test method for hiding power of paints by reflectometry, and was applied to this polyethylene coating sample. The test utilized two spectrophotometric measurements, one coated on black paper and one coated on white paper.

If the coated paper was completely opaque, then the contrast ratio would be 100 percent. The statistical regression model for this data is: contrast ratio =  $20.725 + (2.185 \times [\%TiO_2]) + (1.183 \times [\text{coat wt.}])$ , with

$r^2 \text{ adj} = 0.848$ .

The predicted contrast ratio at 10 percent  $TiO_2$  and 10 lb/ream is 54.4. At 20 weight percent and the same coating weight, the contrast ratio increases to approximately 76.3. The coating weight would have to be increased to 28.5 lb/ream to achieve an equivalent contrast ratio, requiring 40 percent more  $TiO_2$  to achieve similar hiding power. Thinner coatings also translate to faster extrusion speeds.

The ability to achieve higher loads of metal oxide pigments using formulations according to the present invention is very surprising. In a preferred embodiment of a coated article according to the present invention, the coated article has only a single coating of a composition including a polyolefin and a metal oxide

pigment, and said single coating has a metal oxide pigment content of greater than 15 weight percent, based on the weight of the single coating, and more preferably 20 weight percent or higher. In another preferred embodiment, a composition according to the present invention is capable of delivering to a coated sheet or article a top layer of a single coating including 20 percent by weight titanium dioxide on Brown Kraft Paper for an extended period without the formation of die lines. In yet another preferred embodiment, a composition according to the present invention is capable of delivering to a coated sheet or article a top

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layer of a single coating including 20 percent by weight titanium dioxide on white paper for an extended period without the formation of die lines. By "extended period without the formation of die lines" is meant at least 8 hours. In the more preferred embodiments of the invention containing (i) a sulfur containing primary stabilizer and a sulfur containing secondary stabilizer, with or without the high metal oxide pigment loading, or (ii) a zinc or alkali metal salt of a fatty acid as set forth herein, with or without the high metal oxide pigment loading, extrusion onto a coating or as a film can proceed for 8 times longer without the appearance of die lines than the case without (i) or (ii).

15 General stabilizer information:

The oxidation of organic polymers, such as polyethylene, involves the abstraction of hydrogen from the polymer to produce a free radical. A primary stabilizer terminates free radicals by donation of a hydrogen atom. An undesirable feature of their action is the formation of by-products, such as quinones, which may add color to the products in which they are used. A secondary stabilizer typically functions by decomposition of free-radical or peroxidic species formed in the degradation processes. Additional functions may include metal deactivation and regeneration of the primary stabilizer. A review of stabilizers is provided in G. Scott, "Atmospheric Oxidation and Antioxidants", Elsevier, N.Y., (1965).

30 Primary stabilizer categories include alkylated phenols and bisphenols, alkylidene bis, tris, and polyphenols, sulfur containing (e.g., thio and di thio), bis, tris, and polyalkylated phenols and amines.

35 Secondary stabilizer categories include organic phosphites, sulfur containing (i.e., thio) esters, metal salts and metal complexes.

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HALS (Hindered Amine Light Stabilizers) can also be used. HALS exhibit activity similar to both primary and secondary stabilizers.

The preferred stabilizers in this invention are  
5 Santonox®, DSTDP, Hostanox® OSP-1 (tris-(2-tert-butyl-4-thio-(2'-methyl-4'-hydroxyl-5'-tert-butyl) phenyl-5-methyl) phenyl phosphite), Seenox® 412S (pentaerythritol tetrakis (beta-laurilthiopropionate)), and Ultranox® 626.

A combination of primary and secondary stabilizers is  
10 preferred. The amount of primary stabilizer can be greater than, equal to, or less than the amount of secondary stabilizer used.

Chill roll release agents/slip additives:

15 Preferred additives include chill roll release agents or slip additives. More preferred additives in these categories include zinc-, lithium-, potassium- or sodium-containing salts of C6-C36 carboxylic acids, preferably C8-C22 fatty acids, fatty acid amides,  
20 complex esters, fluoropolymers, natural and synthetic waxes and silicones. In one of the more preferred embodiments, the composition according to the present invention utilizes from 1 to 2 weight percent, most preferably 1.5 weight percent, of the zinc or alkali  
25 metal fatty acid salt in the final composition (e.g., the extruded composition) When fatty acid amides are used, the most preferably amount is from about 0.2 to about 0.4 weight percent, and for complex esters such as PETS, the most preferred range is about 0.05 to 0.3  
30 weight percent.

As used herein, unless otherwise specified, the terms "chill roll release agents" and "slip additives" are used interchangeably, unless specifically noted otherwise.

35 The more preferred chill roll release agents or slip additives are fatty acid salts containing zinc,

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lithium, potassium or sodium as the counterion, or non-metal compounds such as pentaerythritol tetrastearate, and n-stearyl erucamide. Pentaerythritol tetrastearate, n-stearyl erucamide, and the alkali metal stearates are the most effective for reducing die line formation and are comparable for die line improvement, although pentaerythritol tetrastearate is less expensive.

General stabilizer, slip, and other additive information is shown in Table 2A-2B.

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Table 2A

Group	Mol wt	Antioxidants	Group	Mol wt	Slips
1		Alkylated phenols	1		Fatty acid amides
	637	Irganox 1098		338	erucamide (Kemamide E)
	531	Irganox 1076		591	N-stearyl erucamide (HTSA#3, Kem E 180)
	421	Lowinox WSP		644	erucyl erucamide (Kemamide E 221)
	341	Lowinox 22M46		536	stearyl erucamide (Kemamide S 180)
	220	Naugard BHT		590	erucyl stearamide (Kemamide S 221)
				593	N-N-ethylene bis stearamide (Kemamide W-40)
2		Polyphenols		341	behenamide (Kemamide B)
	775	Ethanol 330		281	oleamide (Slip-eze)
	784	Irganox 3114	2		Complex esters
	700	Cyanox 1790			PETS
	697	Naugard XL-1			Myerol 18-06K
	383	Lowinox 44B25			
3		Thio polyalkylated phenols	3		Fluoropolymers
					Dynamar FX-9613
	358	Santonox TBM6			
	358	Lowinox TBM6 (Santonox equivalent)	4		Natural and synthetic waxes
	358	Lowinox TBP6 (switch between CH3 and OH groups)			Paraffin (Ross Wax 100)
4		Amines			Montan wax (Hoechst Wax E)
					polyethylene wax #2 (Hoechst PE520)
5		Secondary antioxidants - thioesters			Epolene 43
	683	DSTDP			
	514	DLTDP	5		silicones
	1162	Seenox 412S			200 Fluid
	571	Hostanox SE-10 (co-stabilizer)			4-Z15

Table 2B

Group	Mol wt	Antioxidants	Group	Mol wt	Slips
6		Secondary antioxidants - phosphites	6		Metal stearates
	647	Irgafos 168		607	calcium stearate
	604	Ultrinox 626		877	aluminum stearate
	1465	Irgafos 12		877	aluminum stearate #132
	514	Irgafos 38		632	zinc stearate
				306	sodium stearate
7		Thiophenolic phosphite: (hybrid primary/secondary AO)		290	lithium stearate
	1103	Hostanox OSP-1 (metal deactivator)		591	magnesium stearate
				323	potassium stearate
8		Hindered Amine Light Stabilizers (HALS)		144	sodium benzoate
	2500 avg	Chimassorb 944			
			7		Fatty acid ester
					Almer 103
		Titanium Dioxide Types:			Other Additives
		Anatase Uncoated	8		Acid
		Tioxide APG		284	stearic acid
		Anatase Coated			Base
		Kronos 1014	9	106	sodium carbonate
		Rutile Uncoated	10		Antiblocks
		Dupont R100			diatomaceous earth
					amorphous silica (Imasil A10)
		Rutile Coated			
		SCM RCL188	11		Other Fillers:
		Dupont R104			calcium carboxylate
					zinc oxide

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It will be understood by those of skill in the art in possession of the present disclosure that the times listed on the runs for the experiments set forth in the present specification will be affected by equipment type and size and condition, as well as other experimental conditions.

Referring to Table 1 above, as can be seen for instance by Examples 26, 29-31, 90-100, and 108, generally the presence of aluminum, magnesium, or calcium-containing metal soaps, particularly Al-/Mg-/Ca-containing metal stearates, results in the appearance of die lines in a relatively short time, when compared with preferred embodiments of the present invention. Thus, a preferred embodiment of the present invention is a polyolefin composition having stabilizers and/or chill roll release agents/slip additives and in the essential absence of Al-, Mg-, or Ca-containing metal soaps. By "essential absence of Ca-, Mg- or Al-containing metal soaps" is meant that less than 0.5 weight percent of the aforementioned metal soaps are present. More preferably, less than 0.25 weight percent of these metal soaps are present. Even more preferably less than 0.10 weight percent of Al-, Mg- or Ca-containing metal soaps are present. Most preferably, no Al-, Mg-, or Ca-containing metal soaps are purposefully added to the composition.

As can also be seen in Table 1, particularly Example Nos. 128-130, under certain circumstances the presence of zinc stearate or alkali metal soaps in the formulation provides for extended extrusion without the appearance of die lines. Thus, in a more preferred embodiment of the present invention, the composition is a polyolefin composition having stabilizers and/or chill roll release agents/slip additives and in the essential absence of soaps that do not contain zinc or alkali metals. By "essential absence of soaps which do not

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contain zinc or alkali metals" is meant that zinc or alkali metal soaps may be present in the composition, but that less than 0.5 weight percent of other metal soaps are present. More preferably, less than 0.25 weight percent of other metal soaps are present. Even more preferably less than 0.10 weight percent of other metal soaps are present. Most preferably, no metal soaps, other than zinc stearate and/or alkali metal stearate, are purposefully added to the composition.

Furthermore, the most preferred primary stabilizers are Santonox® or Lowinox® TBM6 (chemically essentially if not exactly the same), or Hostanox® OSP1 (a thiophenolic phosphite); tris-(2-tert-butyl-4-thio-(2'-methyl-4'-hydroxyl-5'-tert-butyl)phenyl-5-methyl)phenyl phosphite); and Lowinox® TBP6.

The most preferred secondary stabilizers are DSTDP, Seenox® 412S (pentaerythritol tetrakis-(beta-laurylthiopropionate)), and Ultrinox® 626.

The most preferred slips are N-stearyl erucamide, PETS, erucamide, N,N-ethylene-bis-stearamide, erucyl stearamide, N-oleylpalmitamide, stearyl stearamide, erucyl erucamide, behenamide, zinc stearate, lithium stearate, potassium stearate and sodium stearate.

Referring again to Table 1, Example 145 showed greatly improved performance for vapor lines, and provided an even coating without the presence of die lines, for at least 660 minutes. Likewise, trials using zinc stearate (Examples 138, 140, 142, 144, and 146) also were particularly noteworthy.

The following additional points can be made based on the experimental data shown above, with respect to additives and their effects on die-related surface defects in a polyolefin composition, particularly polyethylene in combination with a pigment such as titanium dioxide: (1) alkaline earth metal and aluminum salts of fatty acids are widely used as slips and

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dispersion aids for pigmented polyolefins, but they are ineffective for preventing die lines; (2) monoamides of fatty acids (such as stearamide and erucamide) are widely used as slips/lubricants/etc., but they are  
5 ineffective for preventing die lines; (3) bis-amides of fatty acids (such as ethylene-bis-stearamide) are widely used as slips or antiblock agents, but they cause severe moisture line problems and do not prevent die lines; (4) zinc stearate alone or in combination with other  
10 additives was found to give good die line performance when conditions are carefully controlled; (5) phenolic antioxidants alone do not generally provide good die line performance and show, at best, minor improvements in die line performance; (6) phosphite stabilizers  
15 (e.g., Irgafos® 168) in combination with a variety of other additives (e.g., phenolic antioxidants), do not provide good die line performance; (7) a sulfur-containing phenolic antioxidant (e.g., Santonox®) in combination with a sulfur-containing ester (e.g., DSTDP  
20 and Seenox® 412S) provided excellent die line performance, the effect clearly being synergistic; (8) likewise, alkali metal salts of fatty acids (e.g., Li, Na, K) are not commonly used as dispersion aids for pigmented polyolefins but provided excellent die line  
25 performance when used alone or in combination with other additives; (9) the combinations set forth in point (7) and particularly those set forth in point (8) permit extrusions of formulations containing unusually high levels of pigments (e.g., 20 weight percent or higher),  
30 without formation of die lines; and (10) the combinations set forth in points (7) - (9) are effective using both anatase and rutile pigmented formulations, as well as, more generally, formulations containing either coated or uncoated titanium dioxides.

35 Among the many preferred embodiments of the present invention are:

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A composition that can be extruded into a film, extrusion coated onto a substrate, or coextruded with other polymers, and that can be extruded at elevated temperatures for extended periods without the formation of die lines and without the appearance of vapor lines, said composition comprising a base material including at least one polyolefin, and at least one member selected from the group consisting of:

(i) sulfur-containing phenolic antioxidants in combination with sulfur-containing esters;

(ii) zinc or alkali metal salts of fatty acids;

the aforementioned composition wherein the base material comprises polyethylene; the aforementioned composition further comprising at least one metal oxide; the aforementioned composition further comprising at least one metal oxide selected from zinc oxide and titanium dioxide; the aforementioned composition comprising at least one metal oxide selected from rutile and anatase titanium dioxide; the aforementioned composition comprising at least one metal oxide selected from coated grade or uncoated grade; the aforementioned composition further comprising zinc oxide; the aforementioned composition comprising polyethylene, titanium dioxide, and an alkali metal fatty acid salt; the aforementioned composition comprising polyethylene, titanium dioxide, and a sodium salt of a fatty acid; the aforementioned composition comprising polyethylene, titanium dioxide, a sulfur containing phenolic antioxidant, and a sulfur containing ester; the aforementioned composition comprising greater than 15 percent by weight of a metal oxide pigment; the aforementioned composition comprising greater than 20 percent by weight of a metal oxide pigment; the aforementioned composition extruded into a film or extrusion coated onto a substrate; the aforementioned composition with or without stearic acid;

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also an article of manufacture comprising a substrate with an extrusion coating thereon, the extrusion coating comprising a composition according to any of the aforementioned compositions, particularly  
5 wherein the substrate with an extrusion coating thereon is a component of photographic paper, or wherein the substrate with an extrusion coating thereon is a component of thermal imaging paper, or wherein the substrate with an extrusion coating thereon is a  
10 component of digital imaging paper, or wherein the substrate with an extrusion coating thereon is selected from packaging product based on the group consisting of paper and paperboard, or wherein the substrate with an extrusion coating thereon is a component of a soap box,  
15 a milk carton, or a juice carton;

also an article of manufacture comprising a substrate with at least two polymer compositions coextruded thereon, including a first composition closest to said substrate, and a second composition next  
20 to said first composition, wherein said second composition comprises the composition according to any one or more of the aforementioned compositions, particularly wherein said first film has at least a surface thereof, closest to said substrate, at least  
25 partially oxidized, or wherein the surface of the substrate closest to said first composition is at least partially oxidized, and wherein said substrate comprises paper, or wherein said first composition comprises a polymer selected from the group consisting of  
30 polyethylene, polypropylene, propylene copolymers, ethylene copolymers, polyesters, copolyesters, polyamides, and cellulose;

also a process of extruding polyolefins to make an extrusion product including:

35 a first step comprising extruding a first composition comprising at least one polyolefin;

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a second step comprising modifying said first composition by adding at least one member of the group consisting of (i) a sulfur containing phenolic antioxidant and a sulfur containing ester, (ii) a zinc salt of a fatty acid, and (iii) an alkali metal salt of a fatty acid, to make a second composition, and extruding said second composition;

particularly the process wherein the extrusion product comprises an extrusion coated substrate, or wherein the extrusion product is a component of photographic paper, or wherein the extrusion product is a component of thermal or digital imaging paper, or wherein the extrusion product comprises a substrate with a coating on at least a portion thereof, said coating comprising the second composition;

also a process for extrusion of a polyolefin from an extrusion apparatus to make an extrusion product, comprising:

continually extruding a polyolefin having a first composition while monitoring the extrusion product for the presence of die lines, said first composition including polyolefin and  $TiO_2$ ;

modifying said first composition by at least one of the following steps:

decreasing the concentration of metal stearate, if any, in said first concentration;

adding or increasing the concentration of non-metallic slip additive; and

adding or increasing the concentration of polyolefin stabilizer;

to continually extrude a polyolefin having a second composition, while monitoring the product for the presence of die lines;

also particularly a composition or a film or an extrusion coating comprising polyethylene, rutile or anatase  $TiO_2$  with a weight percent of about 5 to about



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20, 4,4'-thio-bis(2-tert-butyl-5-methyl-phenol) with a weight percent of about 0.005 to about 0.05, DSTDP with a weight percent of about 0.01 to about 0.25, and a non-metal slip having a weight percent of about 0.05 to  
5 about 0.5, the non-metal slip selected from at least one of N-stearylceramide and PETS;

also an article of manufacture including a substrate, a layer comprising a first polymer composition and a layer comprising a second polymer  
10 composition, wherein the first and second polymer compositions are coextruded onto said substrate, and wherein said first polymer composition is between the substrate and said second polymer composition, said first composition being selected from the group  
15 consisting of polyethylene and compositions thereof, polypropylene and compositions thereof, propylene copolymers and compositions thereof, ethylene copolymers and compositions thereof, polyesters and compositions thereof, copolyesters and compositions thereof,  
20 polyamides and compositions thereof, and cellulose and compositions thereof, and said second composition comprising a metal oxide pigment containing polyolefin composition according to any of the aforementioned compositions;

25 particularly wherein the metal oxide-filled polyolefin composition is a  $\text{TiO}_2$ -filled polyethylene composition having greater than 15 percent by weight of titanium dioxide and further comprising sodium stearate;

also a composition that can be extruded into a  
30 film, extrusion coated onto a substrate, or coextruded with other polymers, and that can be processed and extruded at elevated temperatures without the appearance of die lines for an extended period of time, comprising a polyolefin, and at least one slip, wherein said at  
35 least one slip is selected from at least one of the group consisting of zinc stearate, alkali metal

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stearates, Kemamide® W-40, PETS, HTSA, and mixtures thereof, said slip present in the amount of .003 to 10 weight percent, based on the weight of the composition;

particularly wherein the composition comprises  
5 titanium dioxide and having a primary stabilizer selected from Santonox® TBMC, Lowinox® TBP6, Lowinox® TBM6, Hostanox® OSP1, or mixtures thereof, and further comprising a second secondary stabilizer selected from the group consisting of DSTDP, Seenox®412S, and mixtures  
10 thereof, wherein said primary and secondary stabilizers combined are present in the amount of 0.003 to 1.0 weight percent;

or more particularly wherein the composition comprises a metal oxide pigment selected from coated and  
15 uncoated titanium dioxide, said metal pigment present in the amount of 3 to 35 weight percent, at least one primary sulfur containing stabilizer and at least one secondary stabilizer selected from sulfur containing ester, wherein said primary and secondary stabilizers  
20 combined are present in the amount of 0.003 to 1.0 weight percent, even more particularly wherein said primary stabilizer is at least one of 4,4'-thio-bis(2-tert-butyl-5-methyl-phenol) and 2,2'-thio-bis-(6-tert-butyl-4-methyl-phenol), and still more particularly  
25 further comprising a slip selected from at least one of N-stearyleurcamide and PETS, and still even more particularly wherein said secondary stabilizer is DSTDP;

and also to any of the aforementioned compositions, films, or coatings comprising a zinc or alkali metal  
30 fatty acid salt in the amount of from .25 to 1 weight percent;

or any combination or permutation of the above.

The invention has been described above in detail with particular reference to preferred embodiments  
35 thereof, but it will be understood that variations and modifications other than as specifically described

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herein can be effected within the spirit and scope of the appended claims. Moreover, all provisional applications cited above are incorporated herein by reference, and all patents, and literature references or  
5 other publications noted above are incorporated herein by reference for any disclosure pertinent to the practice of this invention.

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CLAIMS

We Claim:

- 5        1. A composition that can be extruded into a film, extrusion coated onto a substrate, or coextruded with other polymers, and that can be extruded at elevated temperatures for extended periods without the formation of die lines and without the appearance of vapor lines,  
10        said composition comprising a base material including at least one polyolefin, and at least one member selected from the group consisting of:
- (i) sulfur-containing phenolic antioxidants in combination with sulfur-containing esters;
  - 15        (ii) zinc or alkali metal salts of fatty acids.
2. The composition according to Claim 1, wherein the base material comprises polyethylene.
- 20        3. The composition according to Claim 1, further comprising at least one metal oxide.
- 25        4. The composition according to Claim 1, further comprising at least one metal oxide selected from zinc oxide and titanium dioxide.
- 30        5. The composition according to Claim 1, further comprising at least one metal oxide selected from rutile and anatase titanium dioxide.
- 35        6. The composition according to Claim 1, further comprising at least one metal oxide selected from coated grade or uncoated grade.
7. The composition according to Claim 1, further comprising zinc oxide.

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8. The composition according to Claim 1, comprising polyethylene, titanium dioxide, and an alkali metal fatty acid salt.

5        9. The composition according to Claim 1, comprising polyethylene, titanium dioxide, and a sodium salt of a fatty acid.

10       10. The composition according to Claim 1, comprising polyethylene, titanium dioxide, a sulfur containing phenolic antioxidant, and a sulfur containing ester.

15       11. The composition according to Claim 1, further comprising greater than 15 percent by weight of a metal oxide pigment.

20       12. The composition according to Claim 1, further comprising greater than 20 percent by weight of a metal oxide pigment.

25       13. The composition according to Claim 8, wherein the weight percent of the titanium oxide is greater than 15%, based on the weight of the composition.

14. The composition according to Claim 9, wherein the weight percent of the titanium oxide is greater than 15%, based on the weight of the composition.

30       15. The composition according to Claim 10, wherein the weight percent of the titanium oxide is greater than 15%, based on the weight of the composition.

35       16. An extruded film comprising a composition according to Claim 1.

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17. An article of manufacture comprising a substrate with an extrusion coating thereon, the extrusion coating comprising a composition according to Claim 1.

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18. The article according to Claim 17, wherein the substrate with an extrusion coating thereon is a component of photographic paper.

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19. The article according to Claim 17, wherein the substrate with an extrusion coating thereon is a component of thermal imaging paper.

20. The article according to Claim 17, wherein the substrate with an extrusion coating thereon is a component of digital imaging paper.

15

21. The article according to Claim 17, wherein the substrate with an extrusion coating thereon is selected from packaging product based on the group consisting of paper and paperboard.

20

22. The article according to Claim 17, wherein the substrate with an extrusion coating thereon is a component of a soap box, a milk carton, or a juice carton.

25

23. An article of manufacture comprising a substrate with at least two polymer compositions coextruded thereon, including a first composition closest to said substrate, and a second composition next to said first composition, wherein said second composition comprises the composition according to Claim 1.

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24. The article of manufacture according to Claim

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23, wherein said first film has at least a surface thereof, closest to said substrate, at least partially oxidized.

5        25. The article of manufacture according to Claim 23, wherein the surface of the substrate closest to said first composition is at least partially oxidized, and wherein said substrate comprises paper.

10       26. The article of manufacture according to Claim 23, wherein said first composition comprises a polymer selected from the group consisting of polyethylene, polypropylene, propylene copolymers, ethylene  
15       copolymers, polyesters, copolyesters, polyamides, and cellulotics.

27. A process of extruding polyolefins to make an extrusion product including:

20       a first step comprising extruding a first composition comprising at least one polyolefin;  
      a second step comprising modifying said first composition by adding at least one member of the group consisting of (i) a sulfur containing phenolic  
25       antioxidant and a sulfur containing ester, (ii) a zinc salt of a fatty acid, and (iii) an alkali metal salt of  
      a fatty acid, to make a second composition, and  
      extruding said second composition.

30       28. The process according to Claim 27, wherein the extrusion product comprises an extrusion coated substrate.

35       29. The process according to Claim 28, wherein the extrusion product is a component of photographic paper.

30. The process according to Claim 28, wherein the

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extrusion product is a component of thermal or digital imaging paper.

31. The process according to Claim 28, wherein the  
5 extrusion product comprises a substrate with a coating on at least a portion thereof, said coating comprising the second composition.

32. A process for extrusion of a polyolefin from  
10 an extrusion apparatus to make an extrusion product, comprising:

continually extruding a polyolefin having a first composition while monitoring the extrusion product for the presence of die lines, said first composition  
15 including polyolefin and  $\text{TiO}_2$ ;

modifying said first composition by at least one of the following steps:

decreasing the concentration of metal stearate, if any, in said first concentration;

20 adding or increasing the concentration of non-metallic slip additive; and

adding or increasing the concentration of polyolefin stabilizer;

to continually extrude a polyolefin having a second  
25 composition, while monitoring the product for the presence of die lines.

33. The article of manufacture according to Claim 17, comprising polyethylene, rutile or anatase  $\text{TiO}_2$  with  
30 a weight percent of about 5 to about 20, 4,4'-thio-bis(2-tert-butyl-5-methyl-phenol) with a weight percent of about 0.005 to about 0.05, DSTDP with a weight percent of about 0.01 to about 0.25, and a non-metal slip having a weight percent of about 0.05 to about 0.5,  
35 the non-metal slip selected from at least one of N-stearylceramide and PETS.



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34. An article of manufacture including a substrate, a layer comprising a first polymer composition and a layer comprising a second polymer composition, wherein the first and second polymer compositions are coextruded onto said substrate, and wherein said first polymer composition is between the substrate and said second polymer composition, said first composition being selected from the group consisting of polyethylene and compositions thereof, polypropylene and compositions thereof, propylene copolymers and compositions thereof, ethylene copolymers and compositions thereof, polyesters and compositions thereof, copolyesters and compositions thereof, polyamides and compositions thereof, and cellulose and compositions thereof, and said second composition comprising a metal oxide pigment containing polyolefin composition according to Claim 1.

35. The article according to Claim 34, wherein the metal oxide-filled polyolefin composition is a  $\text{TiO}_2$ -filled polyethylene composition having greater than 15 percent by weight of titanium dioxide and further comprising sodium stearate.

36. A composition that can be extruded into a film, extrusion coated onto a substrate, or coextruded with other polymers, and that can be processed and extruded at elevated temperatures without the appearance of die lines for an extended period of time, comprising a polyolefin, and at least one slip, wherein said at least one slip is selected from at least one of the group consisting of zinc stearate, alkali metal stearates, Kemamide® W-40, PETS, HTSA, and mixtures thereof, said slip present in the amount of .003 to 10 weight percent, based on the weight of the composition.

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37. The composition as in Claim 36, further comprising titanium dioxide and having a primary stabilizer selected from Santonox® TBM6, Lowinox® TBP6, Lowinox® TBM6, Hostanox® OSP1, or mixtures thereof, and  
5 further comprising a second secondary stabilizer selected from the group consisting of DSTDP, Seenox® 412S, and mixtures thereof, wherein said primary and secondary stabilizers combined are present in the amount of 0.003 to 1.0 weight percent.

10 38. The composition as in Claim 36, further comprising a metal oxide pigment selected from coated and uncoated titanium dioxide, said metal pigment present in the amount of 3 to 35 weight percent, at  
15 least one primary sulfur containing stabilizer and at least one secondary stabilizer selected from sulfur containing ester, wherein said primary and secondary stabilizers combined are present in the amount of 0.003 to 1.0 weight percent.

20 39. The composition according to Claim 38, wherein said primary stabilizer is at least one of 4,4'-thio-bis(2-tert-butyl-5-methyl-phenol) and 2,2'-thio-bis-(6-tert-butyl-4-methyl-phenol).

25 40. The composition according to Claim 39, further comprising a slip selected from at least one of N-stearyleurcamide and PETS.

30 41. The composition according to Claim 40, wherein said secondary stabilizer is DSTDP or Seenox® 412S.

35 42. The composition according to Claim 1, comprising a zinc or alkali metal fatty acid salt in the amount of from .25 to 1 weight percent

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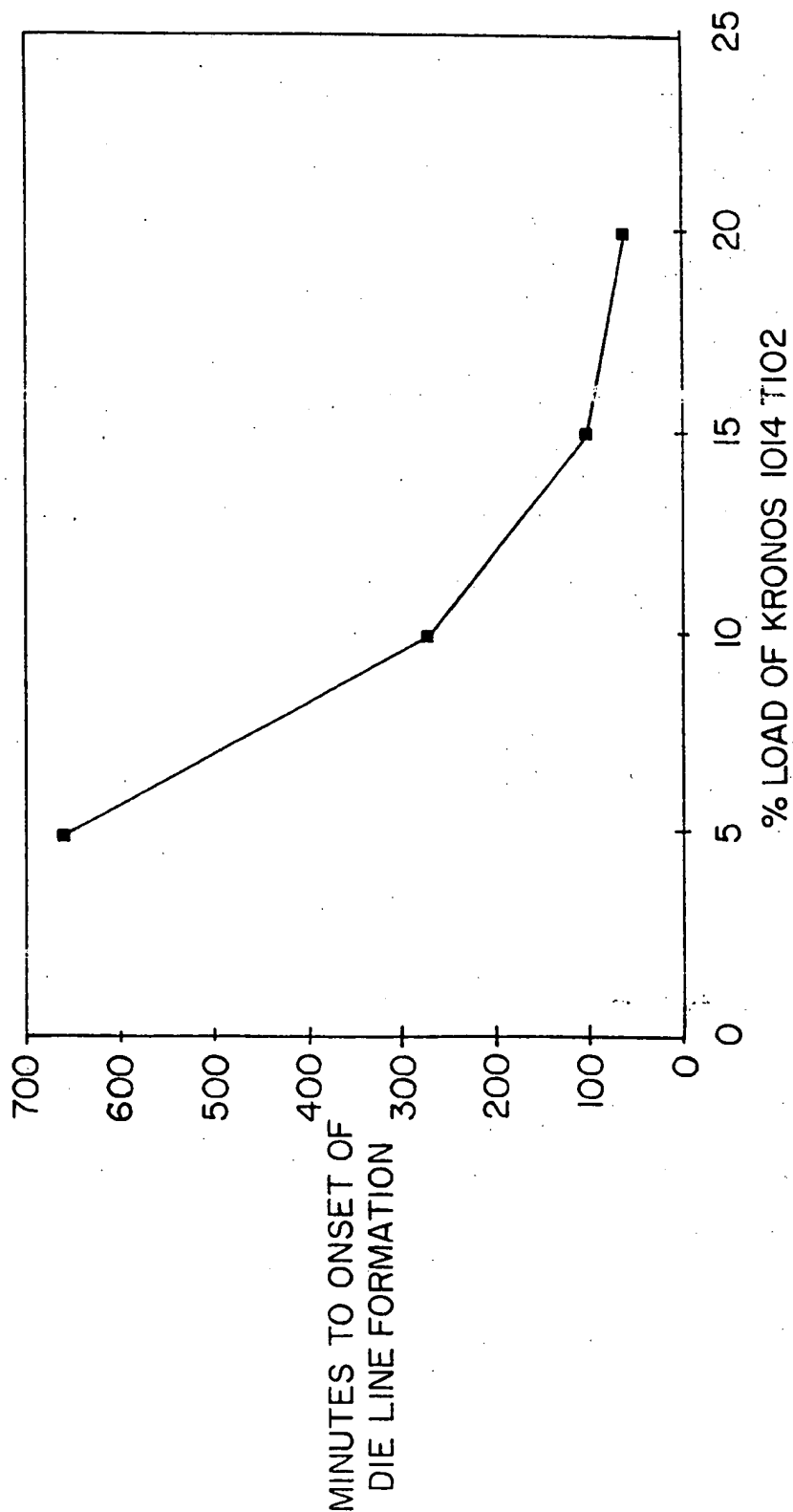


Fig. 1

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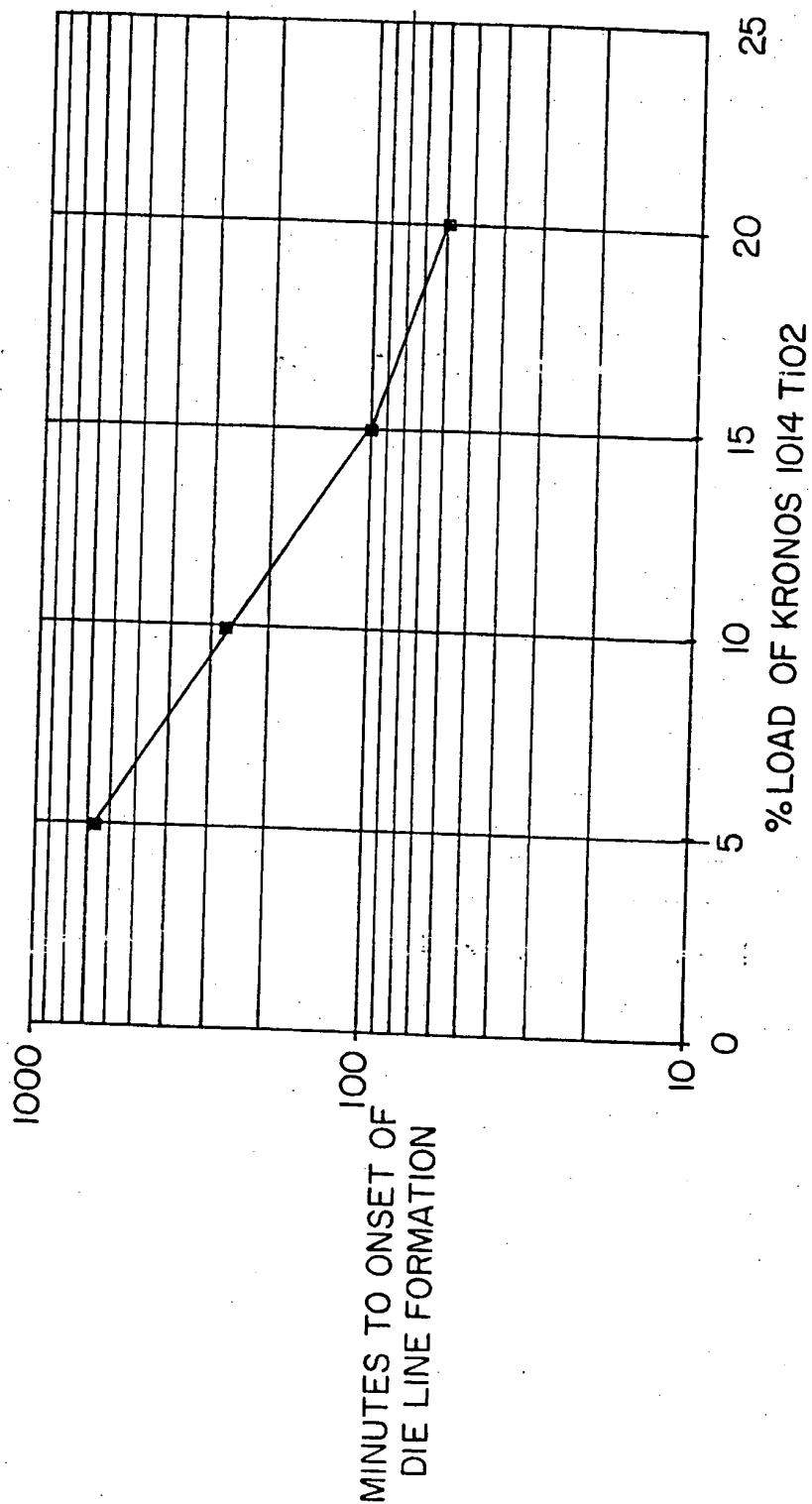


Fig 2

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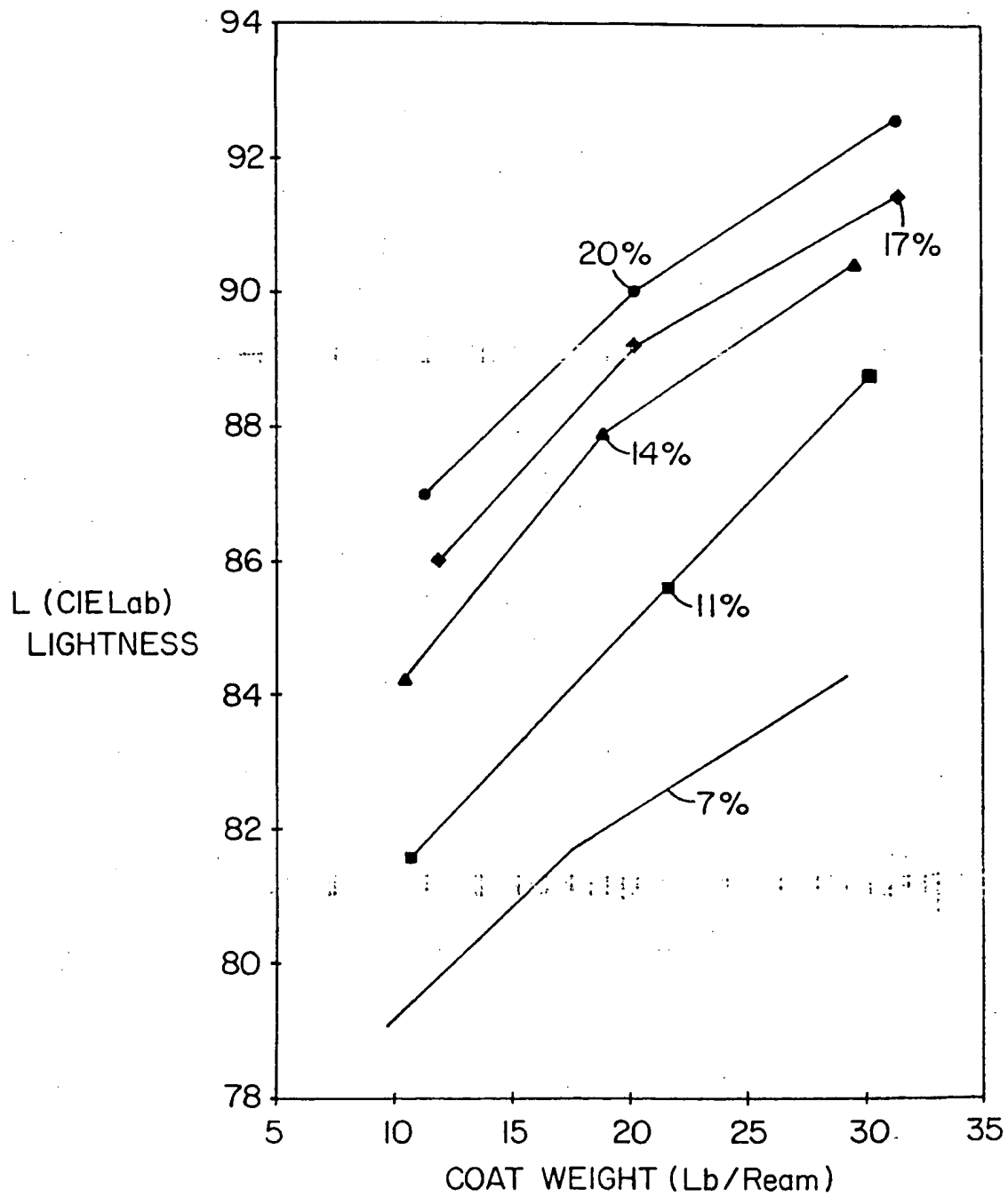


Fig. 3

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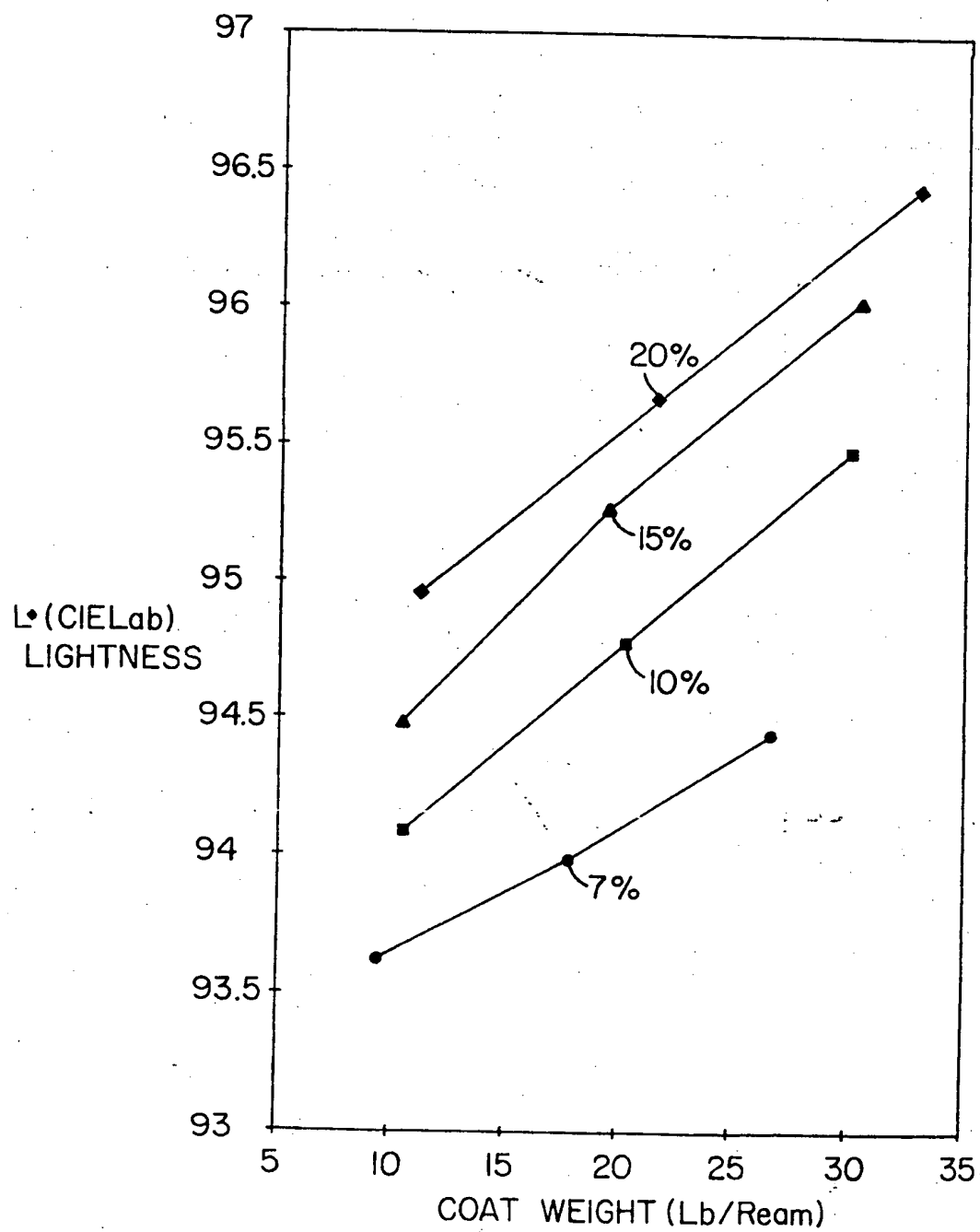


Fig. 4

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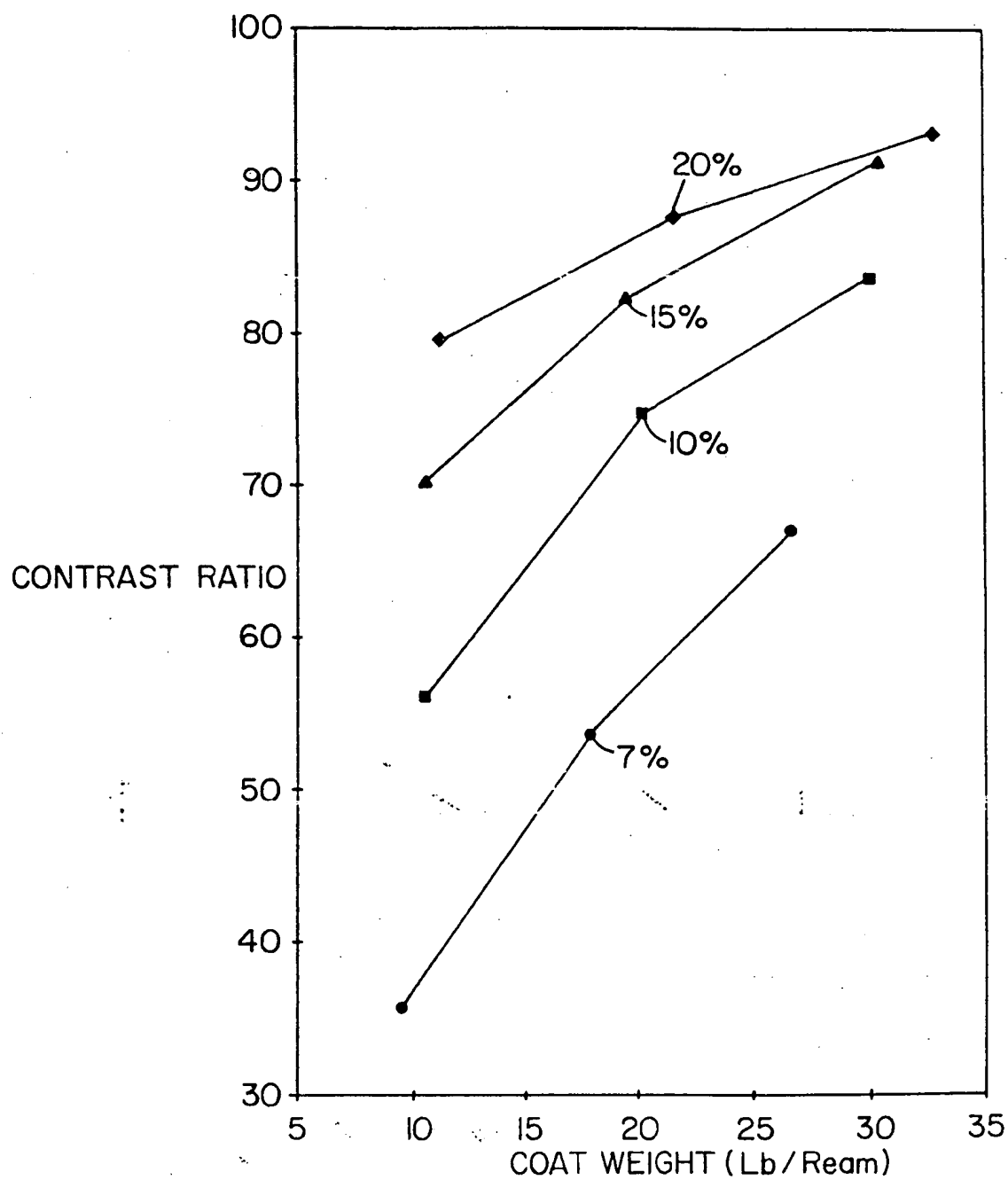


Fig. 5

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/22041

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08K5/098 C08K5/36 C08L23/02 C08J5/18 B32B29/06  
 //(C08K5/36,5:36,5:36)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 450 276 A (PHILLIPS PETROLEUM CO) 9 October 1991 see claims 1,2,8	1,2
Y	EP 0 113 914 A (BASF AG) 25 July 1984 see claim 1	1,2
Y	EP 0 153 867 A (SUMITOMO CHEMICAL CO) 4 September 1985 see claims 1,8,9	1,2
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search

24 March 1998

Date of mailing of the international search report

01/04/1998

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/22041

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI  Section Ch, Week 9031  Derwent Publications Ltd., London, GB;  Class A17, AN 90-235377  XP002060025  &amp; JP 02 163 143 A (IDEMITSU PETROCHEM CO)  , 22 June 1990  see abstract</p>	1,2,16
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X	<p>DATABASE WPI  Section Ch, Week 8338  Derwent Publications Ltd., London, GB;  Class A17, AN 83-768294  XP002060027  &amp; JP 58 136 639 A (MITSUI PETROCHEM IND CO  LTD) , 13 August 1983  see abstract</p>	1,2
X	<p>DATABASE WPI  Section Ch, Week 9330  Derwent Publications Ltd., London, GB;  Class A17, AN 93-239630  XP002060028  &amp; JP 05 162 267 A (CHISSO CORP) , 29 June  1993  see abstract</p>	1,2,16

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Information on patent family members

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